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METHANOL-GASOLINE FUELS
FOR AUTOMOTIVE TRANSPORTATION -
A REVIEW

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16. ABSTRACT

Recent concern for environmental problems and an eventual shortage of conventional petroleum-based fuels coupled with the potential of obtaining methyl alcohol (methanol) as a product of coal gasification has brought about an interest in the use of methanol as a fuel.

In order to assess the feasibility of using methanol as a motor vehicle fuel, either alone (neat) or as a blend in gasoline-type base stocks, its performance, emission and practical use characteristics must be ascertained. To this end this report, which summarizes and evaluates past and current studies concerned with determining these characteristics, is offered. In addition, those performance, emission and practical use consideration characteristics deemed important and found to be lacking in the current technology are identified.

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I. INTRODUCTION

In a survey of the literature by Bolt in 1964 (94)* it was pointed out that alcohol has been promoted as a motor fuel for almost 60 years. Most of the early work was concerned with the use of ethyl alcohol (ethanol) which can be produced by fermentation of grain and other farm products as well as synthetically. The impetus behind these studies was the desire to develop new outlets for farm produce and to develop energy sources other than those based on petroleum. Excess cost and the absence of technical advantages to justify a higher cost prevented the general use of ethanol as a motor fuel (94).

Recent concern for environmental problems and an eventual shortage of conventional petroleum-based fuels coupled with the potential of obtaining methyl alcohol (methanol) as a product of coal gasification (133) has brought about an interest in the use of methanol as a fuel.

In order to assess the feasibility of using methanol as a motor vehicle fuel, either alone (neat) or as a blend in gasoline-type base stocks, its performance, emission and practical use characteristics must be ascertained. To this end this report, which summarizes and evaluates past and current studies concerned with determining these characteristics, is offered. In addition, those performance, emission and practical use consideration characteristics deemed important and found to be lacking in the current technology are identified.

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* Numbers in parentheses designate References listed chronologically in the Bibliography.

II. PAST AND CURRENT STUDIES

In this section, past and current studies concerned with the use of alcohol and alcohol blends as an automotive engine fuel are reviewed. Whenever possible, studies using methanol are used to illustrate a point of consideration. Since there is a paucity of methanol data, the reader will find that many of the studies referred to are concerned with ethyl-alcohol.

The first two subsections, II. A-1, and II. A-2, are concerned with the performance and emission characteristics of straight alcohol-fueled carburetted engines. While blends of alcohol and gasoline are the primary fuels of interest in this study, some of the characteristics obtained from the study of straight alcohol fuels are qualitatively similar to those obtained when alcohol blends are used. Thus the results presented in sections II. A-1 and II. A-2 can be used to make qualitative estimates of trends expected in performance and emission characteristics when blends are used.

In sections II. A-3 and II. A-4 the available literature concerned with the performance and emission characteristics of carburetted engines fueled with alcohol blends are reviewed. The reader will find that many of the works referred to are concerned with ethanol rather than methanol blends. The results presented for ethanol are, for the most part, qualitatively similar to the methanol-blend data.

In addition to knowing the effect of methanol on conventional, carburetted, spark ignition engine performance and emission characteristics, it is important that the effect be known for advanced powerplant configurations which might be in use if and when methanol becomes available as an automotive fuel ingredient. Thus, Sections II. B and II. C have been included. Section II. B describes the limited results obtained with other than carburetted engines. Section II. C describes the results obtained for emission-controlled engines using methanol and methanol-blend fuels.

The measurement of certain exhaust gas species in alcohol blends is troublesome. Section II. D-1 contains a discussion about these emission measurement problems. Section II. D-2 discusses and evaluates various available emission measuring techniques as applied to methanol-fueled engines.

Practical use consideration such as fuel volatility, blend stability, materials compatibility and engine wear are discussed in Section II. E.

II. A CARBURETTED ENGINES

II. A-1 ENGINE PERFORMANCE - ALCOHOL

Various parameters have been identified as being probable causes of the differences observed when the performance of alcohol-fueled and gasoline-fueled carburetted Otto cycle engines are compared. These parameters are considered in the following sections and their theoretical and experimentally observed influences on engine performance characteristics are discussed.

LATENT HEAT OF VAPORIZATION. One of the major differences between the alcohols and gasoline with regard to their use as engine fuels is their latent heat or enthalpy of vaporization. Alcohols have much higher latent heats. For example, the latent heat of vaporization of methanol is 3.4 times that of gasoline on a mass basis [506 vs. 150 BTU/lbm (173)], and, more importantly for combustion engine considerations, 7.5 times on a lower heating value basis [0.059 latent heat BTU per lower heating value BTU for methanol versus 0.0079 for gasoline (173)]. This difference has beneficial as well as detrimental effects on engine operation as discussed in the following sections.

POWER OUTPUT. A beneficial effect of the alcohol's high latent heat is the potential for increased maximum power output attainable from a given engine over that obtained with gasoline. This effect is well known and has been used extensively for racing and aircraft applications. Table 1 contains some power output data for ethanol and methanol.

One of the greatest increases at equal compression ratios reported is that found by Ricardo and Glyde (48). Their data show an 8.2% gain for 190 proof ethanol and a 10.3% gain for methanol as compared to gasoline. A study by Bernhardt and Lee (158) shows a 10% gain for methanol over gasoline in a multi-cylinder Volkswagen engine.

The gain in power output depends on the amount of heating in the induction system. High heating is found to reduce power output (53). Some investigators (125,129) report that the maximum imep* using methanol is about the same or even lower than that obtained with gasoline. These investigators used heated fuel-air mixtures. Ebersole and Manning (129), for example, maintained fuel-air inlet temperatures of 125°F. In all their test cases liquid methanol was either absent or was present only in minor quantities as a fine fog observed through windows installed in the intake manifold, upstream of the intake port of their single cylinder engine. Thus, by heating the mixture, they nullified the evaporative cooling effect of the high latent heat methanol as explained below.

Mixture heating is not the only parameter which influences the relative increase in power of alcohol over gasoline. For example, Rogowski and Taylor (49) showed that for optimum (minimum bsfc @ best power Φ) inlet temperature and spark advance 190 proof ethanol exhibited a lower bmep than gasoline for compression ratios less than 6.6 and a larger bmep for compression ratios greater than 6.6 when a comparison was made with a 70 ON gasoline at 1400 RPM. At 900 RPM the compression ratio at which this reversal occured was 5.5. With a modern high-octane number gasoline this reversal will occur at a higher compression ratio.

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* See Symbols and Abbreviations Section for definition of the commonly used symbols and abbreviations employed in this report.

On a mass basis methanol has a lower heating value than gasoline. A cubic foot of a stoichiometric mixture of air and vaporized methanol, however, has essentially the same heating value as a cubic foot of a stoichiometric mixture of air and vaporized gasoline [94.5 BTU/ft^3 methanol vs. 95.6 BTU/ft^3 gasoline both at 14.7 psia and 60^{o}F (87)]. The reason for the equality is that, while methanol contains less heating value per unit mass, there is proportionately more methanol in a cubic foot of a stoichiometric mixture; the stoichiometric air-fuel ratio for methanol is 6.45, and gasoline $\approx$ 14.5. This equality of volumetric heating value is consistent with the observation described earlier where an engine will produce essentially the same power output when operating on either vaporized methanol-air mixtures or vaporized gasoline-air mixtures.

VOLUMETRIC EFFICIENCY. Increased imep with alcohol is usually attributed to increased volumetric efficiency. Increased volumetric efficiency in turn is attributed to the relatively large decrease in temperature of the fuel-air mixture resulting from the evaporation of the high latent heat alcohol in the intake manifold.

An increase in volumetric efficiency of 5% over that of gasoline is reported by Lichty and Ziurys (33) when neither the 190 proof ethanol-air or gasoline-air mixture was heated. The increase was 7% when both were heated. Ricardo and Glyde (48) report a 6.6% increase in volumetric efficiency at stoichiometric condition for ethanol over that of gasoline. Pye (38) reports an observed 2.3% increase in volumetric efficiency for ethanol over gasoline for stoichiometric and leaner air-fuel ratios. For rich fuel-air ratios the volumetric efficiency of ethanol rose while that for gasoline remained essentially constant; the rise was such that at an equivalence ratio of 1.3 the ethanol volumetric efficiency was 4.3% greater than that for gasoline.

MIXTURE TEMPERATURE. Calculations show that the temperature drop in going from a stoichiometric mixture of air and liquid fuel to air and vaporized fuel in an adiabatic process is about 37°F for gasoline, 246°F for methanol and 143°F for ethanol (Appendix B). If the intake air is 68°F, then the mixture temperature at the end of an adiabatic process involving complete evaporation of a stoichiometric liquid methanol-air mixture will be -178°F. At the partial pressure of methanol in a stoichiometric methanol vapor-air mixture at 1 atmosphere total pressure, the corresponding saturation temperature is 70°F (Appendix B). This temperature is higher than -178°F. Thus, complete evaporation in an adiabatic intake manifold for a stoichiometric liquid methanol-air mixture is thermodynamically impossible since evaporation will cease once the fuel-air mixture temperature becomes as low as the saturation temperature corresponding to the partial pressure of the vaporizing methanol. The degree of evaporation is also limited by the finite heat transfer and mass diffusion rates associated with the evaporation process. Thus, during engine tests the alcohol fuel will be partially in the liquid state at the end of the intake stroke unless there is heat transfer to the mixture in the intake manifold. It is of interest to note that for the same manifold heating required to completely vaporize gasoline, ethyl alchol would be only 54% evaporated (33). The degree of vaporization would be even less for methanol for the same heat transfer.

Lichty and Ziurys (33) made measurements of mixture temperature for 190 proof ethanol in a CFR engine. At stoichiometric fuel-air ratio and no mixture heating, the ethanol mixture was found to be 35°F (19.4°C) lower than gasoline. At maximum power equivalence ratios ($\phi = 1.21$ ethanol, 1.26 gasoline), the temperature was 30°F (16.7°C) lower.

Using an intake-air heater, Rogowski and Taylor (49) conclude that the inlet-air temperature for 190 proof ethanol should be 140°F (78°C) higher than that for gasoline in order to obtain minimum specific fuel consumption at best-power fuel-air ratio. Richardo, who was one of the earliest investigators of the use of alcohols as engine fuel, discusses inlet heating and temperature in (48), which is a summary of his work.

COMPRESSION WORK. Starkman et al. (103) point out that increased volumetric efficiency resulting from the above-described chilled air-fuel charge hypothesis has usually not been substantiated by airflow measurement. They contend – and substantiate with calculations – that the high latent heat increases power output as a result of its decreasing the work during the compression stroke. Their calculations were for the idealized Otto cycle (114) assuming equilibrium combustion products. The effects of chemical reaction rates and heat transfer were not included. They considered two types of fuel-air mixtures: the first was for 100% evaporation in the intake manifold, the so-called dry charge; the second was for no evaporation prior to the closing of the intake valve, the so-called wet charge. For an equivalence ratio of unity the dry charge compression work was 134 BTU/lbm for isooctane and 160 BTU/lbm for methanol. The wet charge compression work was 130 BTU/lbm for isooctane and only 101 BTU/lbm for methanol. Thus a 37% reduction in compression work was calculated in going from a dry to a wet charge for methanol and only a 3% reduction for isooctane.

COMPRESSION STROKE DISSOCIATION. Improved performance has also been attributed to dissociation of methanol during the compression stroke. Such dissociation would lower the temperature after the compression stroke [about $45^{o}F$ ($25^{o}C$) for a 10% methanol blend (143)]. There was some doubt raised concerning this postulate at the 1974 Engineering Foundation Methanol Conference, however, because of the insufficient time for such a dissociation reaction to occur. Additionally, gas sampling after the compression stroke by one attendee did not show any dissociation products to be present.

OTTO CYCLE TEMPERATURES. Another advantage of methanol's high latent heat is that, by its acting as an internal coolant, it lowers temperatures throughout the cycle. As illustrated by the Starkman et al. calculations (103), peak cycle temperatures are reduced from 5100°R (2833°K) to 4870°R (2706°K) in going from a dry to a wet methanol charge. The corresponding reduction for isooctane is only from 5220°R (3067°K) to 5200°R (2889°K).

Even with a fully vaporized fuel the methanol is found to have an advantage of lower peak cycle temperature.

Starkman et al. (103) calculated the peak temperatures to be 5100°R for methanol and 5220°R for isooctane for a fully vaporized fuel.

Bernhardt and Lee (158) computed burned gas temperatures in the post-flame region of the combustion chamber. A two-zone model of flame propagation was used to compute mean burned gas temperature. The burned mass fraction was obtained from a thermodynamic analysis of the engine combustion process. For a 7.88 compression ratio engine operated with a 6% fuel-rich mixture at 3010 RPM, maximum power spark advance, and wide open throttle, the peak temperature of the methanol combustion process was found to be 450°F (250°C) lower than that for gasoline.

Calculations by Adelman et al. (128) also showed lower combustion temperatures for methanol.

In a CFR engine Brooks (52) measured the temperature of a plug screwed into the cylinder head. With ethanol the temperatures were found to be 50 to 70°F (10 to 21°C) lower than with gasoline at a compression ratio of 5.11 over a range of air-fuel ratios.

SPECIFIC HEAT. It has been stated that because of the lowering of cycle temperatures there should be less variation in the specific heat, and thus the alcohol engine should be more efficient* than isooctane. Lichty and Ziurys (33) also point out that the mean specific heats at constant volume, for the range 1000° to 4000°F (556° to 2222°C), for the products per mole of air-fuel mixture are 7.26 and 7.42 respectively for gasoline and alcohol mixtures, thus indicating (neglecting chemical equilibrium effects) a 2.2% higher temperature and pressure rise and thus approximately this much more power output.

MOLAR EXPANSION. The alcohols are reported to have an advantage over isooctane with regard to the ratio of moles of combustion products to moles of reactants. An increase in this ratio should increase power output. Taking into account dissociation and considering a fully vaporized, i.e. dry, fuel at the beginning of the compression stroke, Starkman et al. (103) show a 1% and 2% gain in molar expansion ratio over isooctane for methanol and ethanol respectively. For a wet fuel the gains are 13% and 7% for methanol and ethanol respectively. Data are also presented for no dissociation [see outline of (103) in Appendix E].** Lichty and Ziurys (33) pointed out this effect of molar expansion in 1936.

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* The term efficiency refers to the enthalpy efficiency (114) which is defined as the nondimensional ratio of the work output per cycle divided by the product of the mass of fuel used per cycle times the lower heating value of the fuel.

** Before using information in Appendix E see note on page

EFFICIENCY. Table 2 contains some efficiency data for both ethanol and methanol at equal compression ratio. It is observed that in general, depending on operating conditions, the alcohols exhibit higher efficiencies than gasoline and methanol a higher efficiency than ethanol. Jackson and Tillman (171) report even higher gains in efficiency for methanol than shown in Table 2. They report 18 to 28% less fuel-energy (BTU) consumption at maximum power and 15 to 26% less BTU consumption at road load as compared to gasoline. Also of interest is their observation of a 41% lower BTU consumption at 50 miles per hour cruise when the engine is adjusted to give equal exhaust nitric oxide concentrations for both gasoline and methanol. At 70 miles per hour and equal nitric oxide concentration the BTU consumption is 70% less.

In addition to methanol exhibiting higher efficiencies the peak values are found by some investigators to occur at leaner equivalence ratios than found with gasoline. This occurence is illustrated in Table 3. Ebersole and Manning (129) find peak efficiency to occur for isooctane and methanol at essentially the same equivalence ratio. Their observed lean misfire limits with methanol, however, are approximately 0.2 equivalence ratios leaner than with isooctane. The ability to burn methanol efficiently at lean mixtures results in lower emissions and does not appear to introduce the driveability problems encountered with methanol blend operaation at lean mixtures (159).

DISTRIBUTION. An undesirable feature of the high latent heat of methanol is the fuel distribution problem it presents in multi-cylinder engines. Very little data has been published using straight methanol as a fuel in such engines. It is well known, however, that poor distribution results in significant reduction in power and efficiency and in increased exhaust emissions [Taylor and Taylor (87), Yu (92), Cooper et al. (71)]. Lichty and Ziurys (33) present data which show an increase in 190 proof ethyl alcohol fuel consumption of 14.7% in a multi-cylinder engine as compared to a single-cylinder engine. The corresponding increase for gasoline is only 11.3%. This increase indicates the distribution difficulty associated with the use of high latent heat fuels. Bolt (94) also reports that for multi-cylinder engines the mixtures distribution with 190 proof ethyl alcohol is poor and would probably require a special intake manifold. In Bolt's own tests he saw greater amounts of liquid fuel in the intake manifold of a 6-cylinder Nash engine when ethyl alcohol was used than was observed with gasoline. In tests at the University of Miami with a 4-cylinder engine (155), it was observed that the mixture reaching the front cylinder was at a temperature higher than that of the mixture reaching the rear cylinder. This observation indicated that the distribution of methanol was not uniform. Jackson and Tillman (171) also report poor distribution with methanol in a conventional manifold.

To alleviate the distribution problem Adelman et al.(128), installed a heat exchanger at the carburetor adaptor plate and a heated intake manifold. Initially, engine cooling water was used as the heat source. The heat exchanger proved adequate at idle and low-speed cruise but inadequate at high speed. Use of the heated manifold improved performance and emissions, but maldistribution was still present. A switch to exhaust gas heating was necessary because of the time required for the engine cooling water to reach operating temperature. The exhaust gas heated intake manifold gave satisfactory performance without the use of the heat exchanger. Use of the heat exchanger did, however, make a measurable contribution to HC and CO emissions reduction.

Distribution can also be improved by having the carburetor produce as homogeneous a fuel-air mixture as possible. To this end Bernhardt and Lee (158) altered a standard carburetor to improve the atomization of the fuel. Like Adelman et al., they also equipped their engine's intake manifold with pipes through which exhaust gas flowed. They also used engine cooling water as a heat transfer fluid in the intake manifold.

In the light of the problems of obtaining good distribution with methanol and of the increased power loss, fuel economy loss, and increase in emissions resulting from poor distribution, it is important that primary attention be given to this topic if methanol is to become a practical engine fuel.

FLAME SPEED. Another difference between methanol and isooctane is the relationship between flame speed and equivalence ratio. The relationship is important because it can influence the extent to which the fuel-air mixture can be leaned out without experiencing a drop-off in efficiency. Figure 1, taken from (85), shows the flame speed for methanol and isooctane as a function of equivalence ratio, ϕ. For gasoline it is observed that the flame speed decreases very rapidly as the mixture is made leaner than stoichiometric. This might help to explain why, as described above, isooctane-fueled engine efficiencies start to decrease with decreasing ϕ at relatively high values of ϕ, whereas methanol, on the other hand, which exhibits a relatively high flame speed over a wider range of air-fuel ratios, can be made to run at leaner mixtures without experiencing excessive burning time losses. This characteristic of the methanol engine has been described previously and is illustrated in Figure 2. The load in Figure 2 is very low (15 foot-lb and 1450 RPM), yet the mixture can be leaned out to around $\phi = 0.78$ before the efficiency starts to decrease.

SPARK ADVANCE. The optimum spark advance, which is related to flame speed and ignition delay, will be different from gasoline. Ebersole and Manning (129) found in their CFR engine tests at near stoichiometric equivalence ratios that methanol required less spark advance than isooctane. The amount of retardation for methanol as compared to isooctane varied from 5 to 10 degrees depending on the power output, as shown in Table 4. In contrast to methanol, ethanol-fueled engine optimum spark advance was found to be essentially the same as for gasoline (52, 53). Lichty and Ziury (33) found that a 2 degree greater spark was required for 190 proof ethanol.

The percentage decrease in efficiency and power output was essentially the same for isooctane and methanol when the spark was retarded from the optimum value (125).

FUEL CONSUMPTION. Fuel consumption data are presented in Table 2. With regard to weight fuel consumption (sfc), methanol is at a distinct disadvantage compared to gasoline since its lower heating value is only about 45% that of gasoline. Assuming equal methanol and gasoline efficiencies, this lower value means that the specific fuel consumption, sfc, will be approximately 2.2 times that of gasoline. As a result of the higher efficiencies attainable with methanol, however, the observed specific fuel consumptions are somewhat lower than 2.2 times that of gasoline.

With regard to volumetric fuel consumption methanol is also at a disadvantage compared to gasoline since its heating value per unit volume is approximately 50% that of gasoline. This means that for equal efficiency methanol will achieve only one-half the miles per gallon attainable with gasoline. Increased efficiency improves this slightly. For example, Adelman et al. (128) measured a mpg with methanol equal to 53% of that with gasoline.

OCTANE QUALITY. Alcohols are known for their high octane quality. The generally-accepted value of the research octane number for both methyl and ethyl alcohol is about 106 (173). They are, however, sensitive fuels in that the motor method octane numbers are 92 and 89 for methyl and ethyl alcohol respectively (173). Data could not be found for the Road Octane rating of methanol.

II. A-2 EXHAUST EMISSIONS - ALCOHOL

Emissions of those exhaust gas constituents presently covered by the Federal Emissions Standards - namely carbon monoxide (CO), nitric oxide (NO_x), and total hydrocarbon (HC) - from non-emission controlled, carburetted, spark ignition, methanol-fueled engines are usually found to be less than those emitted from similar gasoline-fueled engines. Theoretical predictions and experimental measurements of these constituents are discussed in the following Sections. In addition, consideration is given to the composition of the exhaust gas organic compounds, including methanol, aldehydes and polynuclear aromatics (PNA). Emissions from emission-controlled engines, fuel injection engines, and stratified-charge engines are considered in Sections II. B and II. C. As will be seen, neat methanol is found to be a very favorable fuel with respect to meeting the Federal Standards.

CARBON MONOXIDE.

Theory: Calculations show the carbon monoxide emissions from carburetted, methanol-fueled engines to be less than those from gasoline (isooctane)-fueled engines. In order to estimate CO emmissions from a methanol-fueled engine Starkman et al.(121) analyzed an ideal Otto cycle with a compression ratio of 9 to 1. The cycle was composed of compression of a nonreacting mixture of fuel and air treated as a perfect gas with variable specific heats. Compression was followed by constant volume combustion to a final equilibrium mixture of combustion gases. Calculation of the equilibrium composition at peak cylinder temperature conditions is highly dependable for predicting exhaust gas NO_x and CO levels (121). At the condition of peak cylinder temperature the concentration of CO was approximately 80% of that found for isooctane at the same equivalence ratio.

Experiment: Experiments have shown exhaust gas levels of CO for methanol-fueled engines to be less than or equal to that for gasoline. Ebersole and Manning (129) and Bernhardt and Lee (158) all found CO levels to approach zero for lean fuel-air mixtures. At increasing fuel-air ratio they found the CO increase to be less than that for isooctane (129) or gasoline (158).

At $\phi = 1$, Pefley et al. (125) found CO concentrations to be much lower for methanol ($\approx 0.125\%$) than for gasoline ($\sim 2.64\%$). Heitland et al. (169) also found CO levels to be lower for methanol at $\phi = 1$; 0.1% methanol vs. 0.5 % gasoline). These results are in qualitative agreement with calculations (159).

Adelman et al. (128) found lower mass emissions(gm/mi) of CO with methanol as compared to gasoline (22.08 gm/mi vs.10.76 gm/mi 72 FTP, cold start). They did this by taking advantage of the lower lean misfire limit of methanol which permitted operation at leaner mixtures.

Ebersole and Manning (129) operated their CFR engine at $\phi = 0.77$ and found reduced CO emissions without a sacrifice in mep or sfc (Table 4); aldehydes were increased, however.

Jackson and Tillman (171) found substantial reductions in CO emissions. At maximum power with gasoline, CO emissions were 12 to 25 times greater than with methanol. Road load CO values ranged from approximately equal at 30 mph to 3 times less than with gasoline at 70 mph. Corresponding equivalence ratios were not presented, but it is expected that the reduction was due to the use of leaner mixtures.

Adt et al. (155) also found CO levels to approach zero for lean mixtures. At stoichiometric conditions CO concentration was higher than that obtained from gasoline-fueled engines. This increase was probably due to the observed cylinder-to-cylinder fuel maldistribution discussed earlier. Ingamells and Lindquist (170) also found CO emissions from methanol to be greater than those from gasoline during a 1972 FTP simulating a 23-minute city driving cycle on a chassis dynamometer. This increase could also be caused by maldistribution.

In summary, both theory and experiments show that CO emissions from methanol will be less than those from gasoline-fueled engines. Good mixture preparation in the intake manifold, however, is essential to obtaining these reductions.

NITRIC OXIDES.

Theory: Theoretical predictions for methanol-fueled engine nitric oxide emissions are lower than those for gasoline (isooctane). In the previously described calculations by Starkman et al. (121) the concentration of NO_x at peak cylinder temperature conditions is found to be approximately 95% as much as that for isooctane at the same ϕ. Ideal Otto cycle, equilibrium calculations by Adelman et al. (128) show the NO concentration to be 79% of that for isooctane at $\phi = 1$. Using the Zeldovich chain reaction mechanism and taking into account the piston movement during the expansion stroke they calculated frozen NO concentrations. At $\phi = 1$ the NO concentrations were 78% and 82% of those for isooctane at 2400 and 3600 RPM respectively. At $\phi = 0.75$ NO levels were found to be 40% and 28% of that from stoichiometric isooctane at 2400 and 3600 RPM respectively.

Bernhardt and Lee (158) report that NO_x formation by way of the reaction $N_2 + O \rightarrow NO + N$ is restrained due to less available atomic oxygen at the lower methanol combustion post-flame temperatures.

Bernhardt and Lee (158) conclude that a mathematical model consisting 1) of a thermodynamic analysis of the engine combustion process based on a two-zone model of flame propogation and 2) of the Zeldovich chain reaction mechanism (131), which is suitable to describe the formation of nitric oxide in a gasoline-fueled engine, is also appropriate for methyl alcohol combustion. Results of calculations presented in (158) for stoichiometric and lean mixtures show NO concentrations to be about 66% of those for gasoline. Calculated peak NO concentrations occur for both fuels at around $\phi = 0.93$ (Appendix E outline of (158)).

Experiment: Bernhardt and Lee's (158) data show multicylinder, methanol-fueled engine exhaust NO concentration levels to be about 79% of those for gasoline at $\phi = 1$, with equal spark advance and wide open throttle. Ebersole and Manning (129) and Pefley et al. (125) found somewhat different results. Their data indicate that relative mass emissions of NO depend on the throttle setting at $\phi = 1$ and mbt spark advance operating conditions. Under these conditions Ebersole and Manning (129) found NO mass emissions from a methanol and a gasoline-fueled CFR engine to be essentially the same at high loads (greater than about 80% of maximum imep) at $\phi = 1$ (see Table 4). For lighter loads NO mass emissions were lower for methanol. For lean mixtures NO levels were found to be lower for methanol at all imep. In agreement with Ebersole and Manning, Pefley et al. (125) also found essentially equivalent NO concentration at $\phi = 1$ and wide open throttle.

As with CO, NO can be reduced by operating methanol-fueled engines at lean mixtures. Adelman et al. (128) did this and found NO mass emission to be an order of magnitude lower than that for gasoline while maintaining adequate performance in their Gremlin. Ebersole and Manning's data (Table 4) also showed NO reduction at $\phi = 0.77$ without sacrifice in mep or isfc.

Jackson and Tillman (171) tested a V-8 engine using methanol as fuel. They found NO_x concentration to be three to four times lower than that for gasoline at road load conditions. They also found that at NO_x concentrations equal to those of a gasoline-fueled engine, methanol BTU fuel consumption was 41% less at 50 mph and 70% less at 70 mph than that of gasoline.

Bernhardt and Lee (159) found NO concentration at WOT and engine speeds greater than 2700 RPM to be about one-half that for gasoline for an engine fitted with a carburetor that gave good driveability and maintained the 14% efficiency gain given in Table 2.

Ingamells and Lindquist (170) found a reduction of NO_x for methanol as compared to gasoline at both stoichiometric and 10% lean air-fuel ratios. The percentage reduction was greater for the lean mixture (22% stoich. vs. 34% for the 10% lean mixture hot start 1972 FTP).

In gasoline engines nitric oxides consist mainly of NO. NO_2 is present in only small amounts. This has also been observed by some investigators using methanol as fuel (159). Adelman et al. (128), however, found substantial amounts of NO_2. This observation raises the problem, with regard to NO_x measurements in undiluted samples, of the possibility of stripping out NO_2 from the sample in the exhaust water condensate. This problem was observed by Finegold and Van Vorst (167) during their testing of hydrogen fueled engines. To eliminate the possibility of stripping out the NO_2 they heated their sample above the dew point.

In summary, both theory and experiments show that, in general, NO_x emission will be less for methanol-fueled than for gasoline-fueled engine operation.

TOTAL HYDROCARBONS.

Experiments: Engine tests show that hydrocarbon emissions are also lower for methanol fuel provided there is proper fuel preparation in the intake system. Caution must be exercised, however, in evaluating total HC data to be sure that a cold bath was not used to condense water vapor from the sample stream being analyzed for HC. Methanol is known to be stripped from the sample in such cases. There is also concern regarding the use of a flame ionization detector (FID) because of the low relative response of the instrument to methanol and no response to formaldehyde (171). These problems are discussed in Section II. D.

Using a gas chromatograph, Pefley et al. (125) found total carbon equivalent mass emissions to be an order of magnitude lower for methanol than for gasoline. Methanol and methane were found to be the major unburned fuel species in the exhaust. Other HC were found only in small concentrations.

Bernhardt and Lee's (158) order of magnitude reduction in hydrocarbon concentration (HC + methanol)* is consistent with Pefley et al.'s data. These data were obtained in a 4-cylinder Volkswagon engine with good driveability; the problems of methanol FID response and stripping by water condensate did not affect the results obtained (159).

Adelman et al (128) report that tests on the FID they used for their Gremlin HC measurements in Cincinnati yielded a relative response of unity. With the 1972 Federal Test Procedure CVS cold start a Gremlin with gasoline fuel yielded total HC emissions (HC + methanol) of 2.34 gm/mi $CH_{1.85}$ Hydrocarbon Equivalent. With methanol fuel a 1.33 gm/mi $CH_{1.85}$ Hydrocarbon Equivalent was obtained.

Ebersole and Manning (129) found lower emissions of HC with methanol but they used a Beckman Model 108A FID, which used an ambient burning chamber temperature. This could have resulted in a stripping of methanol from the sample.

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* Data are usually presented in terms of total unburned HC plus methanol. A preferred way is to report separately the methanol and HC if possible.

Jackson and Tillman (177), using constant volume sampling and accounting for FID response to methanol, found HC concentration (HC + methanol) to be 3 to 4 times lower than that for gasoline at maximum power in a V-8 engine. Concentrations were about the same for each fuel at 30 mph road load. At road load, as the mph increased, HC for gasoline increased while that for methanol remained the same, until at 70 mph gasoline exhaust HC concentrations were about 3 times those for methanol.

In contrast to the above described results Ingamels and Lindquist (170) observed greater unburned fuel mass emissions for methanol as compared to gasoline at both stoichiometric and 10% lean air-fuel ratios. As with their relatively high CO data from methanol, the increased fuel emissions may have been due to unsatisfactory fuel preparation.

Tillman (180) has also shown data which indicate that relative mass emissions (gm/mi) for methanol versus gasoline are not as favorable as relative concentration emission for the two fuels. Whereas maximum power HC concentrations were about three to four times less for methanol, mass emissions were found to be only about two times less.

In summary, data show that total HC emissions will be less for methanol-fueled engine operation than for gasoline-fueled operation provided there is adequate fuel preparation in the intake manifold during steady state and transient operation. Particular attention must be paid to mixture preparation during the warmup stage of engine operation if HC emissions are to be kept to a minimum.

HC AND CH_3OH COMPOSITION.

In the previous section the term total hydrocarbons referred to total unburned HC plus methanol. In this section consideration is given to the relative amounts of each found in the exhaust as well as to the relative amounts of individual HC species.

Experiment: As mentioned earlier, Pefley et al. (125) found the unburned species to be mainly methane and methanol. Other HC and oxygenated hydrocarbons were found in only small concentrations.

Adelman et al. (128) found methanol to be the dominant species. As discussed in the next section, however, aldehyde emission levels were comparable to methanol emission levels for some tests [See outline of (128), Appendix E].

Bernhardt and Lee (158) found methanol to be the major component - 88.4% (weight) of total HC plus methanol-in a sample obtained from the European Test Procedure. They also found comparable aldehyde levels [See the next section and the outline of (158) in Appendix E].

In summary, measurements show the dominant hydrogen-carbon-containing compound in the exhaust to be methanol for a methanol-fueled engine, with high aldehyde emissions in some instances as discussed in the next section.

ALDEHYDES.

Theory: Bernhardt and Lee (158) bring to attention that spectroscopic studies of methyl alcohol flames show cool flame bands at the base of the flame indicating early formation of excited formaldehyde molecules and that from this it has been concluded that formaldehyde is an important intermediate product in the early phase of the combustion of methanol. Based on their gas chromatographic studies, as well as on the assumption that the elementary processes in the chain reactions of methanol combustion are probably the same as in methane combustion, they present a reaction mechanism for methanol combustion. The predominant initiation reaction is

$$CH_3OH \rightarrow CH_3 + OH \quad , \qquad (1)$$

while the only significant oxidation reaction is the formation of formaldehyde via

$$CH_3 + O_2 \rightarrow HCHO + OH. \qquad (2)$$

Experiment: Caution must be exercised in evaluating aldehyde data.

The chromatropic acid method measures formaldehyde (147). The MBTH method is usually assumed to measure total aldehydes, but the method does not include aromatic aldehydes and may measure only partially the C_5 and heavier aldehydes (147). For a more complete determination of aldehydes, the DNPH method is used (147). This method determines the carbonyls-aldehydes and ketones.

Adelman et al. (128) used the DNPH method to measure total aldehydes while formaldehyde was detected by both the DNPH and chromatoropic acid methods. Formaldehyde comprised about 94% of the total aldehydes measured during a CVS cold start test. Formaldehyde mass emissions(gm/mi) were essentially the same for methanol as the average emissions from a pre-1970 gasoline automobile. Total aldehydes were lower, however, being about 80% that of the pre-1970 gasoline automobile.

Using gas chromatographic techniques, Pefley et al. (125) found aldehyde emissions to consist almost exclusively of formaldehyde and acetaldehyde. The formaldehyde concentration varied from a low of 3 to 4 ppm to a maximum of 170 ppm. Acetaldehyde exhibited a wider range of variation from trace values to almost 500 ppm. No definite correlation between the two was found.

Using the MBTH method Heitland et al. (169) found aldehyde concentrations to be approximately 3 times those for gasoline in a single-cylinder engine.

Contrary to the increases in aldehydes observed on switching to methanol fuel as described above, Ingamells and Lindquist (170) report a 17% and an 8% reduction in aldehydes on switching to methanol for cold and hot start tests respectively at a 10% lean air-fuel ratio.

Fuel-air ratio is found to affect aldehyde emissions. In all operating conditions of their CFR engine, Ebersole and Manning (129) found methanol-fueled engine aldehyde emissions to be greater than those for gasoline. At an equivalence ratio of unity they found methanol-fueled engine aldehyde emissions, by the MBTH method, to be anywhere from about 20% to 100% greater than for isooctane, depending on speed and load. For operation with both methanol and isooctane fuels, aldehyde emissions decreased as the equivalence ratio was increased above the lean limit of combustion. At 1000 RPM the aldehyde emissions reached a minimum at $\Phi \approx 1.1$ for both fuels. At 1800 RPM the methanol-fueled engine aldehyde emission level also reached a minimum at $\Phi \approx 1.1$. For isooctane, however, the aldehyde emissions continued to decrease for equivalence ratios up to 1.3, the maximum Φ tested. Their data also showed that methanol-fueled engine aldehyde emissions tended to be influenced more by equivalence ratio than those for isooctane. At an equivalence ratio of unity the aldehyde emissions were unaffected by imep for isooctane, while for methanol there was an increase with decreasing imep (See Table 4).

Pefley et al. (125) also found aldehyde emissions to decrease as the fuel-air ratio was made richer than stoichiometric. Peak concentration of aldehyde was found to occur at $\phi \approx 0.864$. Their results for aldehyde emissions as a function of ϕ appear to be in general agreement with those obtained by Ebersole and Manning (129), who also found aldehyde emissions to increase as the mixture was made leaner than stoichiometric. This is also in agreement with gasoline aldehyde concentration data presented in Reference 109 where aldehyde concentration was found to increase at lean air-fuel ratios. Since aldehydes are probably the result of low temperature combustion reactions (131) which are subsequently quenched part-way through the combustion process, one might anticipate these results of minimum aldehyde emissions at stoichiometric or at slightly richer than stoichiometric mixtures when combustion temperatures are maximum.

Additional data by Heitland et al. (169) also show increasing MBTH aldehydes with decreasing ϕ over the range $0.93 < \phi < 1.25$ in a single cylinder engine. Data by the same authors (158) in a four-cylinder engine show similar trends. Similar to the Pefley et al. (125) data aldehyde levels peaked at a lean value of $\phi \approx 0.78$ for (158) vs. $\phi \approx 0.86$ for (125). For leaner ϕ, that is $\phi < 0.78$ (158), aldehydes were found to decrease slightly.

In addition to fuel-air ratio Pefley et al. (125) also found aldehyde emissions to be a function of spark advance. On the average they were smaller for low spark advance (0 - 10°BTDC).

In summary, aldehyde emissions from methanol-fueled engines are generally found to be greater than those from gasoline-fueled engines and are maximum at lean fuel-air ratios where CO, NO_x and total HC emissions are low.

PNA HYDROCARBONS.

Experiment: Total Polynuclear aromatic emissions from a methanol-fueled vehicle measured during the European (ECE) 4.052 kilometer test procedure with a 1.5 liter, water-cooled Volkswagen engine were found to be very small compared to those from the vehicle when fueled with gasoline [303 mg/test methanol vs. 7035 mg/test gasoline (169)]. The known carcinogen benzo (a) pyrene (B_aP) was found to be only 1.4% of that found with gasoline (3 mg/test methanol vs. 215 mg/test gasoline).

Methanol fuel thus appears to offer a very significant advantage over gasoline with regard to PNA emissions.

II. A-3 PERFORMANCE - ALCOHOL-GASOLINE BLENDS

A number of investigators have studied the use of ethyl alcohol-gasoline blends as an engine fuel. Mixtures have been limited to a maximum of 30% ethanol by volume. Bolt (94) presents a summary of such studies up to 1964. There are also two other papers and seven discussion articles appearing with Bolt's paper. All of these mixture studies are limited to the use of ethyl alcohol. More recently, tests have been carried out using methanol-gasoline blends. In the following sections the performance characteristics of blends are covered.

LATENT HEAT OF VAPORIZATION. Because of the high latent heat of vaporization of methanol [506 BTU/lb, 281 cal/gm (173)] compared to that of gasoline [≈ 150 BTU/lb, 83 cal/gm (173)] blends of methanol and gasoline exhibit latent heats significantly higher than that for gasoline. For a 5% methanol-gasoline blend the latent heat is 169 BTU/lb (93.9 cal/gm). This represents a 13% increase from that for gasoline. The increase for other blends are: 25% for 10% M, 38% for 15% M and 50% for 20% M (See Figure 3). As a consequence, warm-up and distribution with methanol blends will be more of a problem than with gasoline as is discussed later.

POWER OUTPUT. Measurements for ethanol blends show equal if not slightly greater output than for gasoline. Lichty and Phelps (42), from their single and multicylinder tests, conclude that power output with comparable mixture conditions does not change appreciably with the addition of ethyl alcohol to gasoline except where this addition reduces detonation and permits the use of optimum spark advance. (The question of methanol's contribution to increasing octane quality is discussed later).

Bridgeman (29) reports that with the carburetor and spark set for the mean of the optimum values for the two types of fuels, little difference in power, acceleration, or fuel consumption is observed with a 10% blend or even, under many operating conditions, with a 20% blend of ethanol and gasoline.

Jackson's (100) measurements with a single cylinder 8.9 CR engine using injection of a 25% (wt) blend of anhydrous ethanol denatured with 9.1% (wt) methanol showed the torque to be the same as for gasoline when the engine is operated at the same ϕ. He also found during road tests that in order to achieve equal performance the ethanol-gasoline blend-fueled engine must be operated at about the same ϕ as gasoline.

Lawrason and Finigan (101) report that for a 25% E blend with standard carburetion and spark advance the maximum power output was essentially the same as for gasoline in a 1962 Oldsmobile V-8 engine. With the standard carburetor they were able to obtain only a slight (3%) increase in maximum bhp.

Data from Esso Research and Engineering Co., obtained circa 1949 and presented in Reference 122, show an increase in power of 3.4% with 10% E and 4.7% with 25% E blends when the carburetor was not changed but the spark advance adjusted for each fuel. By adjusting the carburetor for maximum power the power increase over gasoline was 3.8% for the 10% E blend and 6.7% for the 25% E blend.

Union Oil Co. data (1970), also presented in (122), show little difference between maximum bhp output with the blend and with representative gasolines with standard carburetor and specification timing in a 1968 Oldsmobile V-8 with a CR of 8.

Some of the early work with ethanol blends describe the increase in power output obtained when blends, made from low octane number gasolines, were employed in engines operating at increased allowable compression ratios. Such observations, in general, are not pertinent for the high octane quality gasolines and the engines currently utilized as will be described under octane quality.

In summary, the general observation is that equal or at best only slight increases in power output are obtained when blends of up to about 25% alcohol are substituted for gasoline in an engine operating at equal equivalence ratios for both fuels. This is not surprising considering that the maximum increase observed with 100% methanol is around 14% (169) at equal equivalence ratio.

If the outputs for gasoline- and methanol-blend-fueled engines are the same at equal equivalence ratios and the primary cause of change in output on methanol addition to gasoline is the blend-leaning effect described in a later Section entitled "Blend Leaning Effect", then whether the output decreases or increases depends on the initial stoichiometry with gasoline. To illustrate the influence of the blend-leaning affect on bmep, Figure 5 has been prepared. It was generated by taking the typical bmep versus ϕ shown in Figure 4, assuming various percentage blend-leaning effects, and calculating the percentage increase in bmep. For example, if initially the unblended fuel (0 % M) is used at $\Phi = 1.0$ then according to Figure 4 the bmep is 94.5% of maximum. For a 10% leaning effect, the resulting Φ with the blend is 0.9 and the corresponding bmep is 84% of maximum. The percentage increase in bmep is thus $100 \times (84-94.5) \div 94.5 = -11.1\%$ as shown in Figure 5 . The change in bmep upon substituting a blend for gasoline is seen to depend on both the original stoichiometry with gasoline and the amount of blend-leaning that takes place when methanol is added to gasoline. An estimate of the mixture leaning caused by methanol addition to gasoline in an unmodified, carburetted engine is given in the Section entitled "Blend-Leaning Effect."

VOLUMETRIC EFFICIENCY. Little data on volumetric efficiency for alcohol blends exist. In the light of the small increases observed for 100% ethanol (anywhere from 2 to 7%, depending on intake manifold heating), it is not surprising that Lichty and Phelps (42) found no consistent increase in volumetric efficiency for 5, 10 and 20%E blends over that for gasoline. This observation is consistent with their reporting of essentially equal power output with these blends. Data were not found for methanol blend volumetric efficiency, but, based on the above consideration, only slight increases, if any, would be expected for blends of up to around 15%M.

MIXTURE TEMPERATURE, HEATING. As a result of the increased latent heat of vaporization of methanol blends, intake manifold blend mixture temperatures for equal heating will be lower than that for gasoline. Measurements by Lichty and Phelps (42) show the mixture temperature decrease in the manifold to be about 4^{o}F (2.2^{o}C) greater than that for gasoline with a 10% E blend for a given manifold heat input; the decrease is 8^{o}F (4.4^{o}C) greater for a 20% E blend. Brown and Christensen found the temperature drop to be 11^{o}F (6.1^{o}C) greater than that for gasoline for a 10% E blend in multicylinder engines (30).

Rogowski and Taylor (49) found minimum sfc at best power ϕ could be obtained if the inlet air was maintained at 100^{o}F (37.8^{o}C) for both gasoline and 10% E and 25% E blends. A 50% E blend, however, was found to require an inlet air temperature of 130^{o}F (54.5^{o}C) to maintain minimum sfc at best power ϕ. Information similar to Rogowski and Taylor (49) for methanol blends was not found in the literature. Since the latent heat of methanol blends is higher than that for ethanol blends(Figure 3) it is anticipated that the methanol blend level requiring air inlet temperatures greater than 100^{o}F will be lower than that found for ethanol blends. The optimum air inlet temperature will also be found to depend on the design of the intake manifold, carburetor atomization characteristics and manifold heat transfer capability. Intake manifold heating and fuel-air mixture preparation during steady state and transient operation are important engine characteristics for methanol blends as will become evident in the remaining discussion.

OTTO CYCLE TEMPERATURES. Lower cycle temperatures predicted and measured for neat alcohol fuels lead one to suspect lower cycle temperature for blends. By interpolating Otto cycle calculations for isooctane and ethanol, in both of which 100% initial fuel vaporization was assumed, Porter and Wiebe (69) estimated that the peak temperatures for a 25%E blend would be about 40°F (22.2°C) lower than those for isooctane over a range of compression ratios from 6 to 12. Peak cycle temperatures, calculated by Texaco(134) from cylinder pressure measurements, however, were only about 8°F (4.4°C) lower than those for gasoline when a 20%M blend was used in a single cylinder RDH engine. During these tests the ignition timing was kept constant (21°BTC) as well as the inlet mixture temperature (200°F) and Φ. The peak temperature was found to occur about 4 crank angle degrees later for the methanol blend. This resulted in higher exhaust waste heat rejection as reflected by the 100°F (55.6°C) higher exhaust gas temperature measured for the blend.

Others have also measured exhaust gas temperatures for alcohol blends. Contrary to the Texaco (134) measurements, Lichty and Phelps (42) found exhaust gas temperatures for gasoline, 10%E and 20% E blends to be approximately the same at equal Φ. The difference between the Texaco (134) and Lichty and Phelps (42) results (aside from the differences in the alcohols used, which would not account fully for the observed differences) is probably due to the fact that the latter adjusted the spark for each fuel, while the former kept the spark intact.

Reed et al. (143) also measured exhaust gas temperatures for 5 to 30%M blends in a number of 1968 to 1974 vehicles. They report an 18 to 270°F (10 to 50°C) decrease in exhaust gas temperature with the blends in all cases. Such reductions may be attributed to the internal cooling effect of the high latent heat of vaporization blends, lower post-flame temperatures, different flame speeds, and/or ignition delay for methanol combustion.

EFFICIENCY. Table 5 contains thermal efficiency data for both ethanol and methanol blends. It is observed that with regard to energy conversion efficiency there is no penalty associated with the substitution of blends for gasoline. In fact, the data show a general increase in efficiency. The increase, however, can be attributed to a leaning of the mixture when carburetion is left unchanged from that used for gasoline. In such instances, the driveability of the vehicle may be impaired. Whether or not this happens seems to be a function of the vehicle gasoline stoichiometry as well as of the methanol blend level. This behavior pattern will be discussed in the section "Driveability."

At ϕ equal to that for gasoline, a condition described as being necessary to obtain good driveability in a modern vehicle, a 10% M blend was found to have the same thermal efficiency as that for gasoline (184). For a 20% M blend the Texaco data (134) indicate a slight ($\approx$ 3%) reduction in efficiency.

The increase in efficiency observed with methanol blends depends on the stoichiometry of the stock gasoline-fueled vehicle. Wigg and Lunt (195) showed that the efficiency increased by about 8% when a 15% M blend was substituted in a 1967 vehicle which operated rich (AF $\sim$ 13) on gasoline. When the blend was substituted in a 1973 vehicle which operated on a leaner mixture (AF $\approx$ 15), the increase in efficiency was only 1%.

Colucci (189) observed a deterioration in efficiency for high-speed driving cycles for a 10% M blend. This effect was also observed by Lawrason and Finigan (101) when they performed road load tests with a 25% E blend, using standard carburetion and ignition timing. The deterioration in mpg relative to gasoline occurred at speeds greater than 70 mph.

As with power output, the change in thermal efficiency seems to be primarily a function of the blend-leaning effect. Assuming this to be the case, Figure 7 was prepared to illustrate the influence of the blend-leaning effect on thermal efficiency.

The typical η versus ϕ curve in Figure 6 was used to generate Figure 7 in the same manner that Figure 5 was developed from Figure 4, as described in the section "Power Output" for blends. As with power output, the influence of blend substitution on thermal efficiency depends on the initial stoichiometry and the blend leaning effect.

FUEL CONSUMPTION. Table 5 shows that the ethanol blend data and most of the methanol blend data indicate a higher fuel consumption on both a mass and volume basis than that of gasoline. Figures 8 and 9 illustrate respectively the increase in sfc and decrease in mpg that would be obtained if the thermal efficiency for the blend equals that for gasoline. A blend yielding a lower bsfc or higher mpg than indicated in these Figures thus exhibits a higher energy conversion efficiency. Heitland et al. (169) have presented such data. They found the mpg with a 15% M blend to be about 8% greater than that found with gasoline. This indicates a 16% gain in efficiency. Reed et al. (176) have also reported maintaining fuel economy in mpg and in some cases an increase in mpg with methanol blends up to about 10% M, thus indicating gains in thermal efficiency. Equivalence ratio data were not presented, but it is suspected that the equivalence ratio was less (leaner) for the blends as indicated by the observed reduction in CO emissions.

DISTRIBUTION. In the light of the increase in the latent heat of vaporization of alcohol blends, distribution problems are anticipated when blends are substituted for gasoline. Data were not found, however, for the effect of methanol blend substitution on distribution per se.

Lichty and Phelps (36) present distribution data, as determined by exhaust port CO measurements in a 1935 six-cylinder engine, for 10 and 20% E blends. Their results show that, in general, the distribution is affected more by engine operating conditions than by the fuel. Under certain operating conditions (viz. 2/3 load, 1000 RPM), however, they found that ethanol addition did result in poorer distribution. The latent heat of vaporization of the 10% and 20% E blends correspond to that of approximately 6% and 11% M blends respectively. The effect of fuel volatility on distribution is of secondary importance compared to the effect of fuel-latent heat for commercial gasoline (114), but the effect has not been studied for alcohol blends. Thus the blends of equal latent heats, for, in addition to the alcohols themselves having different boiling temperatures, ethanol forms azeotropes. Volatility effects are considered further in Section II. E-1.

BLEND OCTANE CHARACTERISTICS. The octane characteristics of methanol blends are similar to those for ethanol blends. When the alcohol is blended with a gasoline having a lower octane value (either Motor or Research) than that of the alcohol, the octane value of the resulting blend is found to be greater than that calculated by taking the volumetrically weighted sum of the alcohol and gasoline octane values. This positive deviation from a linear mixing model calculation is illustrated for ethanol blends in Figure 10 which is taken from Reference 76 . The dashed lines are the calculated values assuming a RON of 106 and a MON of 89 for ethanol. Similar positive deviations have been reported for methanol blends by Texaco (134) and Johnson (186). The ethanol blend data in Figure 10 also show that there is a negative deviation from a linear octane mixing model if the gasoline used to make the blend has a higher or equal Motor octane rating than ethanol. Methanol data presented by Johnson (186) show a very slight position deviation on the order of 1 Motor octane number when methanol (86 MON) is blended with gasolines having a MON of around 87. From the above, it follows that an octane improvement will be found if the gasoline has a lower octane rating than the alcohol with which it is blended.

It is found that the lower the octane value of the gasoline, the greater will be the increase in octane value for the blend. This would follow from a linear mixing calculation. It is also found to be the case in the actual situation with the positive deviation from linear mixing taken into account [viz. Ethanol, Ref. 76 ; Methanol, Johnson (186)] .

It is also found that the blend Research Octane rating increase is greater than that found for the Motor Rating. This difference follows, since the difference between the Research Octane number for methanol [106 (173), 109 (186)] and gasoline [on the order of 85 to 100 (114, 173)] is greater than the difference between the Motor Octane number for methanol [86 (186), 92 (173)] and that for gasoline [on the order of 75 to 88 (114, 173)].

A cause of the above-described differences in octane rating increase as methanol is added is the greater sensitivity of methanol as compared to gasoline A fuel's sensitivity is defined as the difference between the Research and Motor Octane number (RON-MON) of the fuel. The knocking characteristics of a fuel with a large sensitivity will be more dependent on operating conditions than those of a fuel with a lower sensitivity. Data show this sensitivity for a methanol blend to increase with methanol addition from the sensitivity value for gasoline (≈ 5 to 10) @ 0% M to that of methanol @ 100% M [17 (173) to 23 (186)].

When considering practical use, it is important to know whether or not methanol addition will improve Road Octane ratings. Limited data show methanol to have a small effect on the Road Octane rating of a premium gasoline (144). When gasolines are road rated it turns out that today's vehicle octane requirement is closely related to the Motor Rating. If the same situation is found to exist for methanol-blend-fueled vehicles, then methanol will not be as beneficial for increasing Road Octane ratings as would be the case if the Research method were found to be more closely related to the Road Octane requirements. In fact, if it turns out that satisfactory road performance with methanol blends require Motor Octane values greater than around 90, methanol addition will decrease the octane quality of a base gasoline that originally meets the greater than 90 Motor Octane requirement.

DRIVEABILITY. The substitution of an alcohol blend for gasoline results in a leaner mixture if there are no adjustments made to the carburetor. The extent to which this blend-leaning effect affects performance apparently depends on the stoichiometry used for the gasoline fuel. For lean gasoline operation the effect will be more pronounced than that for rich operation. This characteristic can be explained by consideration of Figure 4 which illustrates the effect of air-fuel ratio on bmep. For rich operation with gasoline (e.g. point e) the bmep is found to be only mildly influenced by stoichiometry. For leaner operation (e.g. point f), however, the bmep is found to decrease more rapidly as the mixture is made leaner.

Some of the earlier studies with ethanol blends report that driveability was not impaired by ethanol addition. This is not surprising as vehicles were operated on rich ($\phi > 1$) gasoline-air mixtures at the time. Egloff and Morrell (32), however, concluded in 1936 that greater fuel flow would be required to maintain the same acceleration when ethanol blends were stituted for gasoline. More recent literature surveys also conclude that driveability in general will be impaired unless adjustments in carburetion are made upon switching to alcohol blends (122 ,144). Whether or not a particular vehicle will require adjustment appears to depend on its stoichiometry with gasoline.

Jackson (100) reports that it is necessary to operate 25% (wt) E blend-fueled cars at stoichiometry equal to that for gasoline to obtain equivalent performance. An increase in surge was noted in each of two 1963 vehicles tested without carburetor adjustment. The increase, however, was not the same for both. Car B, which became commercially unacceptable because of the surge, was found to have a much leaner average stoichiometry (AF $\approx$ 16.7) than car A which operated near stoichiometric air-fuel ratio (AF $\approx$ 14.7).

Texaco (134) found that substitution of a 20% M blend for gasoline in both a 1970 and a 1971 car resulted in poor performance. During steady state operation with gasoline, at other than idle condition, the 1970 vehicle's equivalence ratio was lean, approximately 0.98. For the 1971 car the equivalence ratio under the same operating conditions was also lean, varying between 0.89 and 0.97. For the 1970 car Texaco found that good performance could be achieved by simply enlarging the carburetor main metering jet. Similarly achieved improvement could not be attained with the 1972 vehicle.

Ingamells and Lindquist (170) performed driveability tests with six 1971 vehicles operating on gasoline and 10% M blends. Driveability demerits for all vehicles were found to be greater for the blends when the vehicles were used for commuting at temperatures between 39°F and 70°F (4°C and 21°C). The increase, however, was not the same for all vehicles [see Appendix E outline of (170)]. In fact, with the blend the driveability was still acceptable in two cars. Three of the cars with reasonable driveability on gasoline exhibited poor driveability with the blend and one car deteriorated from poor to very poor driveability on substitution of the blend. Thus, gasoline-fueled cars which already have driveability problems caused by the use of lean stoichiometry will probably become unacceptable upon the use of methanol blends. It appears, however, that some cars which do not exhibit driveability problems on gasoline may be acceptable when the blends are substituted, at least for the range of temperature tested. Chassis dynamometer driveability tests were also carried out with three vehicles at a lower temperature, 24.8°F (-4°C). For two of the vehicles, driveability became worse at this lower temperature when using gasoline, and for the other, driveability became better. On switching to the 10% M blend, two of the vehicles exhibited a much larger increase in driveability demerits as compared to that found on switching fuels at the higher temperature commuting tests. For the third vehicle, however, the increase in driveability demerits on switching to the 10% M blend was less than that found for the higher temperature tests. In fact, there were less driveability demerits for the blend than were found at the higher temperatures. Caution must be exercised in comparing the low temperature and high temperature data, however, for as the authors point out, the test procedures were different for the two.

Reed et al. (143) report that for up to 20% M blends good driveability was maintained in a 1969 Toyota. While explicit fuel-air ratio measurements were not presented, the CO mass emission data for the vehicle showed a 60% reduction, thus indicating stoichiometric or richer gasoline-air mixtures.* In the same vehicle some hesitation was noted for a 30% M blend under idling conditions, and the vehicle was unpleasant to drive with a 50% M blend.

Volkswagen has also tested a vehicle with a 15% M blend and found driveability to be acceptable (159). Similar to the Reed et al. (143) data, they found an approximately 60% reduction in CO emissions, thus indicating stoichiometric or richer equivalence ratios with gasoline.

Colucci (184) reports that driveability is impaired with methanol blend substitution, especially for a 1974 vehicle.

In summary, it appears that the driveability of cars operating near stoichiometric or rich equivalence ratios on gasoline will be acceptable on substituting methanol blends, but cars operating lean on gasoline will exhibit deterioration in driveability. Cars already exhibiting driveability problems with gasoline will become worse when methanol blends are substituted.

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*See Section II. A-2.

BLEND LEANING EFFECT. Texaco (134) has presented blend leaning effect data for both a 1970 and a 1971 car. With a 20% M blend, they found a reduction in Φ of between 0.07 and 0.2 units for the 1970 car and between 0.08 and 0.15 units for the 1971 car. The amount of reduction was a function of operating condition. In the 1970 car, the greatest change was at 20 mph road load condition while for the 1971 vehicle it occured at idle.

The changes in Φ observed by Texaco (134) are in qualitative agreement with calculations presented in Appendices C and D, where the reduction in Φ resulting from the substitution of a methanol blend for isooctane is estimated. In the calculation it is assumed that the carburetor discharge coefficient (114) remains the same for both the blend and isooctane. The calculations show a decrease in Φ of approximately 0.12 units on switching from isooctane at stoichiometric fuel-air ratio to a 20% M blend. Figure 11 illustrates the results of such calculations for up to 100% M blends. The vertical axis is the blend leaning effect parameter used in Figures 5, 7, 13, 15 and 17, while the horizontal axis is the % M blend. These results are approximations and should be used accordingly.

As reported by Bolt et al. (123), the carburetor discharge coefficient does not remain constant. It is influenced by many factors including the fluid mass flow rate, specific gravity, viscosity and surface tension. Also, the change in fuel flow rate resulting from variations in fluid properties, is, in general, different for each geometry and pressure differential. The report states that appropriate choice of metering orifice geometry can diminish the influence of fuel-property variation. This indicates that, for vehicles requiring carburetor enrichment on switching to blends, satisfactory operation might be achieved by merely enlarging the metering jets. Texaco (134) was able to do this in a 1970 car over a rather narrow range of operation (idle and level road load to 50 mph). Over this range the metering characteristics with the enlarged jets and 20% M blend were similar but slightly leaner than those for gasoline. As was pointed out by Texaco (134), however, tests were not conducted to determine if similar-to-gasoline metering characteristics would be found over the vehicle's entire operating range. They pointed to the potential complications associated with two-phase flow in the emulsifier section of the carburetor which are not very well defined. Carburetor metering characteristics were more complex in the 1971 vehicle which Texaco (134) tested. Simply enlarging the metering jets did not yield the same metering characteristics when 20% M blend was substituted for gasoline.

II. A-4 EXHAUST EMISSIONS - ALCOHOL-GASOLINE BLENDS

In the following section comparisons are made between the exhaust emissions from methanol-blend-fueled engines and from gasoline-fueled-engines. There appears to be consensus in the literature that the changes in CO, total HC and NO_x emissions resulting from the substitution of blends for gasoline in a carburetted engine are brought about mainly by the blend leaning effects. Measurements at similar equivalence ratios for blends and gasoline show essentially the same CO, total HC and NO_x emission levels. A difference in emission levels, however, should be found at high concentrations of methanol blends, for 100% methanol fuel is found to exhibit different emission levels when compared to gasoline at the same . Volatility also affects emissions (Section II. E-1).

Gruen at Porsche AG (191, 192) has found CO, total HC and NO_x emissions from a multicylinder methanol-blend-fueled, fuel injection engine to be different from those found when gasoline was used in the engine even at the same equivalence ratio. He also found these emissions to be a function of fuel composition at equal equivalence ratios in a single cylinder engine with inlet pipe fuel injection (145). The reason for the differences between the results of Gruen and others is not clear. For multicylinder engines it could be a result of the better distribution Gruen probably had by using fuel injection. This would not, however, explain the differences observed by Gruen in his single cylinder engine tests.

If the blend leaning effect is the primary cause of the change in emission levels, then whether an emission specie will increase or decrease will depend on the initial stoichiometry with gasoline. To illustrate this, typical curves of CO, total HC and NO_x emissions versus equivalence ratio have been used as a basis to make predictions of emission level changes. The results are shown in Figures 12 through 17. For example, Figure 12 shows the relationship for CO emission versus ϕ as obtained by Ninomiya (119) for methanol blended with toluene, isooctane and normal heptane. Figure 13 illustrates the changes in CO emissions resulting solely from blend-leaning effects. Figure 13 was generated by selecting various blend-leaning effects and determining the percentage decrease in CO. For example, if initially the unblended fuel (0%M) is used at $\phi = 1.1$, then according to Figure 12 the CO emissions are 3.5%. For a 5% leaning affect the resulting equivalence ratio with the blend is $0.95 \times 1.1 = 1.045$, and the corresponding CO emission level from Figure 12 is 1.75%. The % reduction is thus $100 \times (3.5-1.75)\ 13.5 = 50\%$ as shown in Figure 13. Figures 12 through 17 should be referred to when reading the following section on CO, total HC and NO_x emissions.

In addition to making comparisons with gasoline emissions per se it is also important to compare methanol-blend emission data with the Federal Standards. Some gm/mi data measured during various driving cycles are presented in Table 6. For the methanol blend levels presented it is apparent that unless the emissions with gasoline satisfy or come close to satisfying the Standards, the blends will not satisfy them either. In other words, blending with methanol does not appear to be a very useful method for achieving the Federal Standards. This conclusion is made for 20% or less methanol blends. Since neat methanol was found to be a very favorable fuel with respect to meeting the Federal Standards, much higher methanol-concentration blends should exhibit similar characteristics. There are, of course, other problems related with high concentration blends as discussed elsewhere.

CARBON MONOXIDE. Data presented for methanol blends (95, 119, 134) show that when CO emissions for methanol blends are compared with those for gasoline at the same , there is no difference between the two. It should be pointed out, however, that these investigators made CO measurements in single-cylinder engines. It is possible that the CO emissions for methanol blends in multicylinder engines could be higher than those for gasoline at equivalence ratios near unity if geometric distribution problems in the intake manifold arise, for it is known that such maldistribution can increase CO emissions (131).

When blends are substituted for gasoline without adjustment to the carburetor, the mixture becomes leaner. For modes of operation where the gasoline-air mixture is near stoichiometric and richer, this blend-leaning effect will result in a decrease in CO emission concentration. For lean gasoline-air mixture operation, however, there will be no significant reduction since the CO concentration reaches and maintains a constant low level for such stoichiometry (Figure 12). Thus, a vehicle operating with a specified average stoichiometry on the rich side will exhibit a larger reduction in CO than a vehicle with a leaner average stoichiometry when a methanol blend is substituted for gasoline and no changes are made in carburetion. This has been observed by Reed et al. (143) who found the ratio of decrease of CO mass emission with methanol addition to be the greatest for vehicles with initially high levels of CO, that is, for vehicles with rich gasoline stoichiometry [see outline of (143) in Appendix E; also refer to Figure 13.]

Methanol will thus be effective in reducing CO emissions from vehicles which can operate on methanol blends with good driveability at leaner than gasoline-fueled operation stoichiometry. Modern emission-controlled vehicles which operate at lean stoichiometry and exhibit driveability problems even with gasoline will not perform satisfactorily with blends unless the carburetor is adjusted, thus negating the CO reduction benefit from the blend-leaning effect. Catalyst-controlled vehicles, however, operate at richer stoichiometry and should exhibit less driveability problems, though the leaner mixture may make the catalyst less effective.

NITRIC OXIDES. As with CO emissions, data presented for alcohol blends (95,119,143) show that when NO_x emissions are compared with those for gasoline at the same there are no differences between the two. An exception is the data of Jackson (100) which show an approximately 6 to 10% increase in NO_x emission concentration when a 25 % (wt) E blend is substituted for gasoline in a single-cylinder engine. The observation of similar NO_x levels at equal ϕ for gasoline and methanol blends is consistent with the observation by Texaco (134) of essentially equal peak cycle temperatures for the two fuels.

The blend-leaning effect of methanol addition to a vehicle with unchanged carburetion can result in either a decrease or increase in NO_x level. The direction of change depends on the stoichiometry utilized with gasoline operation. This is illustrated in Figure 15 where it is observed that leaning of the mixture can result in increased NO_x concentration if the original stoichiometry is richer than that for maximum NO_x production. Conversely, initially lean stoichiometry results in a decrease in NO_x as a result of the blend-leaning effect. The equivalence ratio at which maximum NO_x production occurs is leaner than stoichiometric [$\phi = .94$ (119)]. This dependence of NO_x emissions on gasoline stoichiometry has been reported by Wigg et al. (187). They found an increase in NO_x mass emission when a 15% methanol blend was substituted for gasoline in a 1967 vehicle. In a 1973 vehicle a decrease was observed.

When Texaco (134) substituted a 20% M blend for gasoline in a 1970 vehicle, they observed a reduction in NO_x. The performance, however, became poor. In order to regain the original gasoline performance they had to enlarge the jets as discussed earlier. While NO_x data are not presented for the enlarged jets, CO emissions were found to be essentially the same as those for gasoline. Thus, the NO_x emissions were probably raised to the initial level found with gasoline.

From the above considerations a conclusion regarding the effect on NO_x emissions of substituting methanol blends for gasoline can be made which is similar to the one made for CO emissions. Substitution of blends will reduce NO_x levels only if the vehicle will give satisfactory performance with mixtures leaner than used during gasoline-fueled operation. The extent to which the mixture must be leaned to realize a reduction in NO_x emissions can be greater than that required for reducing CO emissions. This is the case if the initial gasoline stoichiometry is richer than that for maximum NO_x production.

The above statements are made based on data obtained for blends of up to about 25% M. Since lower NO_x levels are found with meat methanol fuel, larger methanol concentration blends may show a corresponding decrease in NO_x even when comparisons are made at equal .

TOTAL HYDROCARBONS. As with neat methanol, caution must be exercised in measuring total hydrocarbons(HC) because of the potential stripping of methanol from the exhaust sample and the lower relative response of the FID to methanol. Gas chromatographic (GC) analysis of a 20% M blend by Texaco (134), however, indicates rather low levels of methanol in the exhaust, thus making these measuring errors of smaller magnitude than is found with neat methanol fuel.

At equal equivalence ratios total hydrocarbon emissions appear to be the same for methanol blends and gasoline when comparisons are made for lean mixtures. This was observed by Texaco during its GC analysis. For equivalence ratios less than around 0.95, a 20% M blend produced the same volume concentration of total hydrocarbons as gasoline. Ninomiya et al. (119) found that as the equivalence ratio was decreased (made lean) the effect of methanol on the exhaust hydrocarbons gradually subsided. At an equivalence ratio of 0.8, methanol addition to the fuel had no effect on hydrocarbon emissions.

For richer mixtures, the affect of methanol substitution for gasoline on total HC emissions is not clear. Texaco (134) found that for Φ greater than about 0.95 a 20% M blend produced lower total HC emissions than gasoline at equal equivalence ratios. Conversely, for a 20% M blend Ninomiya et al. (119) found an increase in total HC. They attributed the increase to the fuel decomposition inhibition resulting from the presence of additional formaldehyde found at fuel-rich conditions.

For gasoline, total HC emissions are found to decrease as the equivalence ratio is reduced. This decrease continues until a critical equivalence ratio is reached. The critical equivalence ratio is about 0.8 for conventional auto engines. Leaning of the mixture beyond the critical equivalence ratio results in an increase in HC because of problems associated with incomplete flame propagation. If methanol blends exhibit the same total HC emissions at equal-to-gasoline equivalence ratios, then the addition of methanol will cause a decrease in total HC emission as a result of the methanol's blend-leaning effect. There will be a upper limit to the reduction however. The lower limit will be determined by the extent to

[illegible] be leaned before the hydrocarbon emissions begin to rise. Data are in qualitative agreement with the above. Texaco (134) found an approximately 23% reduction in total HC emissions measured during a Federal test procedure (FTP) hot cycle when 20% M blend was substituted for gasoline. There was a corresponding reduction in equivalence ratio from about 0.98 to 0.83 (for 20 to 50 mph road load operation). Poor driveability was experienced as a result of this lean mixture. On enlarging the carburetor main jets, the equivalence ratio was increased to about 0.95. The total HC emissions increased to a value about 11% greater than that for gasoline. Pefley (183) also found a reduction in total HC during constant volume sampling (CVS) hot start driving cycles. There was a corresponding reduction in CO. However, with CVS cold start tests, he found the HC to decrease with the blend even though CO emission increased. Measurements reported by Shell (183) for a 1970 vehicle undergoing a 1975 FTP show the opposite effect from those data described above, in that the total HC increased even though the CO emissions were lower for the blend.

While the data are not conclusive, it appears that changes in total HC emissions for a vehicle with good fuel preparation are caused to a large extent by the blend-leaning effect. The change is a function of the vehicle tested, and the primary vehicle parameter governing the change is its stoichiometry with gasoline. Figure 17 is offered as a qualitative prediction of change in total HC emissions for various degrees of blend leaning as a function of stoichiometry with gasoline, resulting solely from the blend-leaning effect. Volatility also affects HC emissions as is discussed in Section II. E-1.

HC and CH_3OH COMPOSITION. The emissions data currently available in the open literature show that hydrocarbon composition changes with methanol addition and that methanol itself is present in the exhaust.

Data from Ninomiya et al. (119) are presented in the Appendix E outline of (119). The fuels used were blends of isooctane, normal heptane and toluene. The toluene concentration was maintained at 50% by volume while the isooctane and normal heptane concentration were varied to maintain a Research Octane number of 93 for the various methanol blends tested. As discussed in the previous section, methanol addition was found not to affect exhaust hydrocarbons at lean equivalence ratios ($\phi < 0.8$). The individual species hydrocarbon data presented are for a rich mixture with $\phi = 1.18$. Of importance is the change in exhaust gas hydrocarbons relative reactivity. The data show a definite increase in reactivity for methanol addition of greater than around 15%, 'or lower than 15% M there is no change in reactivity, while for a 20% M blend the reactivity increases by about 13%, and a 40% M blend resulted in an approximately 39% increase. The increase in reactivity is attributed to the rise in unburned toluene levels.

Data from Texaco (134) are also presented in the Appendix E outline of (134). In contrast to the Ninomiya et al. (119) data, the Texaco measurements were taken at stoichiometric air-fuel ratio, and the Texaco data is for 20% M blended in a commercial gasoline. Also, the Texaco data are presented on a volume concentration basis (ppm C_6) and the Ninomiya et al. data on a mass of emission per mass of the assumed fuel source of the individual exhaust specie. There are differences in the results obtained. Whereas Ninomiya et al. found a slight (≈ 1%) increase in toluene for a 20% M blend, Texaco found a decrease (≈ 13%). While Texaco observed a 49% decrease in methane concentration, Ninomiya et al. found only a 17% decrease in methane (assumed formed from all fuel components) for a 20% M blend. This disparity between the two results would be even greater if comparisons were made at the same equivalence ratios because the effect of methanol addition on the Ninomiya et al. (119) data as discussed above would become less at lean mixture and the methane decrease would be less than 17%. Texaco also found a rather large decrease in acetylene (57%), while Ninomiya et. al (119) found approximately the same acetylene per pound of toluene in the fuel with a 20% M blend, the volume fraction of toluene in the fuel being kept constant at 50%.

Wigg and Lunt (187), during the 1975 FTP, also measured individual hydrocarbon concentrations for a rich-operating 1967 vehicle, a lean-operating 1973 vehicle and a 1973 vehicle with a catalyst. They found that the presence of methanol in the blend led to relatively small changes in exhaust aromatic and olefin content with no consistent trends apparent. The change in hydrocarbon reactivity was found to be affected more by the change in hydrocarbon mass rate of emissions than the change in composition. For the rich-operating 1967 vehicle, there was little change for a matched RVP blend but a significant increase in reactivity for the non-matched RVP blend. Little change in reactivity was observed for the 1973 catalyst-equipped vehicle, though an increase was noted for the non-matched RVP blend.

With the limited available data it is difficult to make generalized statements regarding the effect of methanol addition on relative reactivity and hydrocarbon species found in the exhaust. It can be said, however, that the concentration of methanol found in the exhaust will be greater than that found when gasoline is used as the fuel.

ALDEHYDES. There is consensus in the limited available literature that aldehyde emissions increase when methanol is used as a fuel constituent (119, 122, 188).

Ninomiya et al. (119) found the formaldehyde volume concentration to increase 70% (from 17.6 to 30 ppm) at an equivalence ratio of 1.17 when a 25% M blend was substituted for the toluene /isooctane /normal heptane-blend discussed in the previous section. They attributed the increase to the incomplete combustion of methanol according to the following route:

$$CH_3OH + O_2 \rightarrow \dot{C}H_2OH + H\dot{O}_2$$

$$\dot{C}H_2OH + O_2 \rightarrow CH_2O + H\dot{O}_2 \ .$$

In the presence of formaldehyde, alkyl radicals derived from the hydrocarbon fuel can undergo chain transfer

$$\dot{R} + CH_2O \rightarrow \dot{C}HO + RH$$

which would inhibit oxidation of saturated hydrocarbons (119). The transfer results in the increased total hydrocarbon emissions discussed in the previous Section. The effects of formaldehyde on exhaust hydrocarbon levels disappear for lean mixtures since, in the presence of excess oxygen, the reaction of formaldehyde with oxygen is faster than the chain transfer with alkyl radicals (119).

Esso Research and Engineering Company has presented aldehyde emission data in gm/mi as found while testing three vehicles with gasoline and a 15% M blend with the Federal Test Procedure (190). The results are contained in Table 6. There was an increase in aldehydes for all vehicles. Of interest is the very large increase observed when the car was initially operated lean on gasoline. This increase resulted from the previously described increases in aldehyde levels observed for lean mixtures.

More data regarding aldehyde emissions from blends are needed before generalized statements can be made, other than that they are found to increase over those from gasoline.

POLYNUCLEAR AROMATICS. Volkswagenwerk AG (159) made measurements of polynuclear aromatic (PNA) emissions from a VW Dasher (Passat LS) fueled with gasoline and a 15% M blend during the European (ECE) test procedure. With gasoline the total PNA emissions over the 2.518 mile test procedure was 1070.4 μg. This PNA emission level is quite low for gasoline - fueled operation. A more typical value is around 20,000 (159). When the 15% methanol blend was substituted for gasoline the PNA emission level dropped to 888.5 μg. This represents a 17% decrease in PNA emissions.

Benzo (a) pyrene, a known carcinogen (147), decreased by an even greater amount. The reduction was from 3.1 μg with gasoline-fueled operation to 2.3 μg with the 15% M blend. This represents a 25% reduction.

The above-described data are included at the end of the Appendix E outline of (158). PNA emission data from the Dasher fueled with neat methanol are also included.

II. B NON-CARBURETTED ENGINES

II. B-1 FUEL INJECTION ENGINES

In order to help alleviate the starting, warmup and distribution problems encountered with methanol it has been suggested that fuel injection be employed (128). Gruen at Porsche AG has done so (191). He has used up to 20%M blends in an unmodified production vehicle without experiencing driveability problems. With gasoline the fuel-air ratio was stoichiometric. The blend substitution resulted in an approximately 9% leaning effect. There was a 75% reduction in CO emissions, a 30% reduction in total HC emissions and a 22% reduction in NO_x emissions. These reductions are greater than would be expected from solely blend leaning effects (191). This suggests that methanol blend substitution is advantageous for fuel injection engines from an emissions standpoint. More tests are needed, however, to confirm this postulate. Cold starting was not investigated under extreme conditions but for temperatures between 32^{o}F (0^{o}C) and 68^{o}F (20^{o}C) no problems were encountered. They are anticipated, however, at lower temperatures.

R. Tillman of the Continental Oil Company, as described at the EPA Symposium (197), has converted a 1972 fuel injection Volkswagen to operate on both gasoline and methanol. This dual-fuel capability was achieved by installing an extra set of fuel injectors so that there were two injectors per cylinder. With gasoline operation, one set was used, with methanol both sets. At the time of the Symposium (197), the vehicle was still in the developmental stage, but preliminary data indicate the conversion method to be a promising one.

II. B-2 STRATIFIED CHARGE ENGINES

Lange et al, have tested methanol in the Porsche SKS stratified-charged engine (193). Other data by Porsche are presented in (192). As would be expected from the decreased heating value of methanol, the brake specific fuel consumption was found to be about 2.2 times that found with gasoline at essentially equal equivalence ratios. The optimum ignition timing was essentially the same as that for gasoline operation. This similarity of timing is in contrast to the retarded optimum ignition timing usually found for conventional engine methanol-fueled operation. In qualitative agreement with tests made with conventional engines, both CO and NO_x emissions were found to decrease even at equal equivalence ratios. The reduction in CO was between 50 to 70% over a wide range of mean effective pressures. nitric oxide reductions were the greatest at higher loads when a richer mixture was used. The HC data are inconclusive because of the problems associated with their measurement during methanol-fueled operation. In Appendix E the above-described data are given. The hydrocarbon values presented with methanol-fueled operation are described as bing about 30% lower than actual. If this is the case, then the HC emissions with methanol operation are higher than those with gasoline operation at light loads and are smaller at high loads.

Porsche has also operated a stratified-charge engine with methanol fuel in the prechamber and gasoline in the main combustion chamber. An advantage of thsi technique is easier control of fuel flow to the prechamber, resulting from the increased volume flow requirements of methanol as compared to gasoline. The prechamber volume of the Porsche engine was about 8 to 12% of the main chamber volume. At equal equivalence ratios the efficiency and optimum ignition timing were the same as for gasoline operation while the specific fuel consumption was greater. For total $\Phi > 0.65$ the NO emissions from the methanol-gasoline operating mode were greater than those for gasoline operation; the opposite was found for $\Phi < 0.65$ (lean mixture). CO emissions were lower for the dual fuel

This is in contrast to methanol-gasoline blend data derived during conventional engine testing, where the emissions are usually the same at equal equivalence ratios. It is of onterest to note that the CO emissions from the dual fuel operating mode were the same as those found during straight methanol operation for $\Phi > 0.59$. HC emissions were higher for the dual fuel operation. The above described data are presented in the Appendix E outline of (193).

II. C EMISSION-CONTROLLED ENGINES

II. C-1 METHANOL-FUELED ENGINES

EXHAUST CATALYSTS. Catalytic oxidation treatment of neat methanol-fueled engine exhaust gas is an effective method of lowering unburned fuel emissions. This effect has been demonstrated by Adelman et al. (128). They found the methanol exhaust gas content to be reduced from 1580 ppm without the catalyst to 161 ppm with the catalyst during a 1972 FTP cold start test. For a hot start test the corresponding reduction was from 810 ppm to 29 ppm. This result represents an average 93% reduction in unburned methanol concentration. They also found FID total HC mass emissions to be reduced by 86% during a '72 CVS cold start test.

Ingamells and Lindquist (170) also found substantial reduction in unburned fuel when a catalyst and air injection were employed with a methanol-fueled engine. The unburned fuel mass emissions were found to decrease 94%, similar to the magnitude of reduction observed by Adelman et al. (128).

Aldehydes, the other major exhaust-gas carbon-hydrogen containing species, are also found to be reduced by an oxidizing catalyst. Adelman et al.(128) found an average 78% reduction in total aldehyde concentration emissions. The reductions were from a level of 155 ppm to a level of 36 ppm for the '72 CVS cold start test and from 144.8 ppm to 29.2 ppm for the hot start.

Carbon monoxide emissions from methanol-fueled engines are also lowered by exhaust gas catalysts. Adelman et al.(128) found a 70% reduction in mass emissions during a '72 CVS cold start test. Ingamells and Lindquist found a 94% reduction during a '72 hot start test.

In addition to catalytic converters it has been reported that there is the potential of controlling methanol-fueled engine exhaust with lean thermal reactors.

II. C-2 METHANOL BLEND-FUELED ENGINES

EXHAUST CATALYSTS. Wigg and Lunt (187) have found the CO, HC and NO_x emissions from a 15% methanol blend-fueled catalytically controlled 1973 vehicle to be essentially the same as those from gasoline-fueled operation.

The same vehicle exhibited low MBTH aldehyde emissions with both fuels when the Reid Vapor Pressures (RVP) of the fuels were matched by backing out all the butane and half the pentanes from the base gasoline before adding the methanol. The levels were 0.002 gm/mi for the gasoline and 0.004 gm/mi for the 15% M blend. When the RVP was not matched the higher RVP, 15% M blend exhibited much greater MBTH aldehyde emissions. The values measured were 0.006 gm/mi for gasoline and 0.02 gm/mi for the blend.

Catalytically emission-controlled vehicles which satisfy the Federal HC, CO, and NO_x standards with gasoline are anticipated to satisfy them with methanol-gasoline blends. More data are required before a general statement can be made regarding aldehyde emissions from such a vehicle, but it is anticipated that they will be higher than the aldehyde emissions found during gasoline-fueled operation.

EXHAUST GAS RECIRCULATION. While no data were found regarding the affect of EGR on methanol blend fueled-engine NO_x emissions, it is anticipated that the effect will be similar to that found for gasoline-fueled operation.

II. D EMISSIONS MEASUREMENTS

II. D-1 PROBLEMS

CO, CO_2, NO, NO_2. The analysis of CO, CO_2, NO and NO_2 has generally been standardized throughout the past few years. The methods presently employed involve continuous real time non-dispersive infra-red (NDIR) analyzers for CO and CO_2 and chemiluminescent detectors for oxides of nitrogen. A dispersive infra-red (DIR) CO, CO_2, and NO detector has been described by Lord et al. [1].* Their results are in good agreement with the NDIR detectors. In addition, a dispersive NO analyzer (DNO) need not be preceded by a desiccant. The DNO analyzer also compared favorably with the chemiluminescent analyzer. Although some investigators have used "wet" methods of analysis such as the Saltzman method (129, 134) and a modified phenol disulfonic acid method (101) for NO_2 determinations, the chemiluminescent detector has the major advantage of speed and simplicity as well as accuracy.

Since the NDIR, DIR, DNO, and chemiluminescent analyzers all have been shown to be reliable for these measurement, the adoption of any one of these methods for CO, CO_2, NO, and NO_2 seems to be acceptable. Caution must be exercised, however, if an exhaust gas water condenser is used because some of the relatively large amounts of NO_2 found by some investigators in methanol-fueled engine exhaust will be stripped out with the water. A heated sample will avoid this problem with the vacuum-type reaction chamber chemiluminescent analyzer.

HYDROCARBONS. For gasoline-fueled engines, the flame ionization detector (FID) has been accepted as the method for determining "total exhaust hydrocarbon emissions." The FID has been termed a carbon-counting device because the response due to hydrocarbons is proportional to the rate of introduction of carbon into the flame. Two moles of ethane produce close to the same response as one mole of butane. The chemical nature of the sample molecule, however, influences the effectiveness of the carbon atom in producing the flame response. Thus, due to this structural effect observed, the term effective carbon number is used in comparing the molar response of molecules to the FID. Most hydrocarbons have effective carbon numbers nearly equal to the number of carbon atoms found in the molecule. In general, this is true for aromatic compounds, but olefins show a decreased response (carbon number > effective carbon number) and acetylene an increased response (carbon number < effective carbon number).

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*Numbers in brackets denote References listed with their numbers

Fortunately, exhaust gases appear to contain relatively equal amount of olefins and acetylenes, a condition which tends to cancel out the effects of different molar response. Thus, it is generally accepted that the gross FID response will reflect a total carbon equivalent and therefore a "total hydrocarbon emission" yield.

If methanol-fuel engines are used, methanol itself appears as a major component in the exhaust. The effective carbon number of methanol to the FID has been obtained by Sternberg et al.(2); it is 0.75. Ackman (3) has reported a calculated value of 0.55, while Dietz (4) obtained a value of 0.52. Adelman et al. (128) used an effective carbon number of 1.0 for methanol during their investigation but recognized that this value introduced an error in total hydrocarbon emissions based on total FID response. Ebersole and Manning (129) determined the effective carbon response from a molecule of methanol to be 0.85. Jackson (100) noted a difference in the FID responses for hydrocarbon emissions when compared to a NDIR - Hydrocarbon analysis method for an ethanol-gasoline fueled engine, a difference attributed to a lower FID response to ethanol.

The oxygen interference effect (synergism) encountered in the case of measuring gasoline-fueled engine emissions with the FID must also be considered when methanol or methanol-gasoline blends are used. Two approaches have been followed to correct the FID response when O_2 is present in the analyzed gas sample. The first is a method of adjusting the FID fuel to contain a mixture of 40% H_2 + 60% He (131). A second approach is a modification of the FID to include a secondary air inlet (5). Both methods seem to compensate for the O_2 synergistic effect.

It may be noted here that certain FID systems are designed for low temperature operation. This design may result in condensation in the flame tip of the FID producing both excessive noise and operation difficulties. A heated FID (minimum 125°C) appears to correct this difficulty.

A means of removing water from the sample when an unheated FID is used involves an "in line" condensing trap. Raw exhaust gases are passed through a trap and either cooled to dry ice temperature (-80°C) or, as is more usually done, to the melting temperature of water (0°C). In this manner, H_2O is removed from the hydrocarbon, rendering the heating of the FID unnecessary. Unfortunately, this procedure adversely affects the analysis of total hydrocarbon produced from methanol or methanol-gasoline blend-fueled engines, as methanol itself would be at least partially extracted from the sample. Exhaust components with high molecular weights would also be withdrawn in the process to some degree, which would lead to a further lowering of hydrocarbon yields.

Sampling of exhaust gases even for "in line" analysis must be carried out through heated teflon or stainless steel tubing (5) in order to insure representative exhaust analysis.

A second major method of analysis for total hydrocarbons involves the "complete" analysis of the emission through gas chromatology (GS) or gas-liquid chromatography (GLC). Numerous researchers (2, 6-9, 135, and 151) have used one or both of these methods as a supplement to the FID total hydrocarbon analysis. A variety of columns, conditions and methods have been employed for the "complete" analysis of hydrocarbons in exhaust gases. A review of these is not necessary, but a few problems might be noted.

A "complete" analysis of the hydrocarbon emission is extremely time-consuming and requires careful sampling methods. Lassen et al. (7) report 199 peaks in the emission chromatograph, identifying nearly 75%. This emission was taken from a gasoline-fuel engine. FID detection was used due to its high specific response to hydrocarbons. If a "complete" analysis is carried out, total hydrocarbon emissions would be the sum of all hydrocarbon yields.

Sampling techniques for complete analysis require the retention of the sample in the vapor state. It is generally done through heating the sample container and/or the dilution of the sample with an inert gas such as Helium. The major problem encountered is a decrease of the vapor concentration due to the absorption of certain components onto the walls of the sampling container. In general, though, this problem is minor for the hydrocarbon fraction in exhaust gases but is of prime importance for oxygenates.

A complication for methanol-fueled or methanol-gasoline-fueled engines is an expected increase in oxygenated organic molecules which would produce an increased difficulty in the identification of the gaseous emissions.

METHANOL-ALDEHYDES AND OTHER OXYGENATES. The analysis of methanol in the exhaust emissions is of major concern in studies of methanol-fueled engines. As discussed earlier, methanol demonstrates a reduced effective carbon number toward the FID. This introduces an apparent low total hydrocarbon emission yield. Since methanol has been established as a major emission product in methanol fueled engines (128, 129, 158) and is present in blend exhaust (170), determination of methanol emission must be carried out as a part of total hydrocarbon analysis. Although methanol emission has been determined by discontinuous delayed time GC methods, it has not been carried out with continuous real time methods. At present, when no analysis for methanol per se is carried out, the fraction of methanol in the exhaust gases relative to total hydrocarbon is assumed to be identical with the ratio of methanol to gasoline in the fuel.

A second major concern in the analysis of exhaust emissions for methanol-fueled engines lies in the aldehyde content of the exhaust. Presently two major methods are employed to determine aldehyde emission values, the "wet" and the GC(GLC) methods.

The major "wet" methods employed utilize a colorimetric analysis of a 3-methyl-2-benzotheozolenehydrozone (MBTH) derivative (135) of the aldehyde or the 2,4-dinitrophenylhydrozone (DNPH) derivative (135). Both methods involve passing raw exhaust gases through a solution of the reagent for an extended period of time, removal of the solution, preparation of the sample derivative, and finally an analysis by colorimetry. The MBTH method suffers from a decreased response to aromatic aldehydes.

A major modification has been carried out in the case of the DNPH method. Wiggs, et al. (135) collected the DNPH-aldehyde derivative through extraction with cyclohexane. After preparation, this sample was separated through GLC, and individual aldehydes were identified. Oberdorfer (109) determined total aldehydes through the DNPH method, using a gravimetric technique in place of the photometric.

Recently Witt [10] extensively examined the straight gas chromatographic analysis of exhaust gases for aldehyde using a FID and Porapak T column. This method, though somewhat time-consuming, appears most promising.

There appears to be no known method to determine total aldehydes in exhaust gases on a continuous real time basis. All analysis requires considerable time or relatively large sample size. An approach which definitely has great promise has been made through GLC.

Other oxygenated compounds such as ketones have been reported as components in exhaust gases. This class of compounds may be examined and analyzed through standard GLC techniques.

II. D-2 TECHNIQUES

A general discussion of the presently employed methods for the analysis of exhaust gases is given in section II-h. A brief summary of the advantages and disadvantages of these methods as applied to methanol or methanol-gasoline-fueled engine exhaust analysis is given below.

CO, CO_2, NO, AND NO . These methods, as discussed in section II-h, are, except for the problem of losing NO_2 in condenser baths, nearly standardized and need no further discussion in this section.

TOTAL HYDROCARBON. The measurement of total hydrocarbon can be broken down into three (3) method classes: Infrared (NDIR-DIR), FID, and GC-GLC. NDIR and DIR techniques take advantage of the C-H stretching frequency of the hydrocarbon observed in the infrared (IR) region of the electromagnetic spectra. These methods require a calibrating gas similar in composition to the exhaust gas to be measured. Since the absorption of IR is characteristic to the whole molecule, it is structure-dependent. Both the wavelength and the intensity are affected. Thus, this method should require extensive calibration. On the other hand, the IR methods are in general insensitive to interference from other molecules. IR further has the advantage of "in line" real time analysis.

The FID, like the IR, is a continuous real time analysis method. As discussed earlier (Sect. II-h) problems here have been observed with noise levels if the FID is not heated to 120° C or higher. The FID response is also molecular structure-dependent and is in general a carbon analyzer. Most hydrocarbons follow a response profile which is equal to the number of carbon atoms in the molecule. Oxygenated molecules (such as methanol) show reduced response to FID and therefore introduce a serious problem in methanol-fueled engine exhaust analysis. Since methanol is expected to be a major contribution to total hydrocarbon emission, an independent analysis system must be employed in order to correct FID response to reflect total hydrocarbon emissions. The presence of oxygen in exhaust gases affects the FID response, but through addition of Helium to the FID fuel (H_2) or through a modification of the FID detector, this problem can be overcome.

A second major disadvantage of the FID total carbon analysis system is its failure to distinguish the nature of the exhaust components with regard to environmental reactivity. It further fails to detect changes that might occur in the distribution of light-to-heavy hydrocarbon exhaust gases during a test run. In general though, this method is acceptable as a measure of total hydrocarbon emissions for gasoline-fueled operation.

GC and GLC techniques are able not only to obtain total hydrocarbon emission but to specify individual components and changes in components during test procedures. Unfortunately, it is not an "in-line" real time analysis system and cannot be used as a continuous monitoring method. It is extremely time-consuming, requiring time both in the analyzer and in data evaluation. It is, however, a substitute method to the IR or FID that permits a greatly expanded picture of the nature of exhaust gases.

METHANOL, ALDEHYDES AND OTHER OXYGENATES. Presently there are two methods for the determination of methanol in exhaust gases. The first is an approximation method which assumes the percentage of methanol in exhaust gases is equal to the percentage of methanol in the fuel used. The second requires a GC or GLC off-line analysis. Some research is now under way to examine exhaust gases by using IR (either NDIR or DIR) specific for methanol. These methods seem most reasonable and are likely to lead to "in-line" real time continuous analysis systems. At present, though, GC-GLC analysis is the only reliable method.

As discussed earlier (section LL-h), aldehydes may be analyzed by "wet" chemical means with either the MBTH or the DNPH methods. The MBTH method suffers from a low sensitivity factor for aromatic aldehydes. Neither method is capable of real time continuous monitoring, and both require a large sampling of exhaust over a relatively long period of time. Both methods are time-consuming. Also, NO_2 interferes with the methods. Both are primarily "total" aldehyde analysis methods, though the MBTH can be modified so that individual aldehydes can be separated and determined.

Gas Chromatography methods have been employed but also suffer from sensitivity problems (specific to formaldehyde) and from the long time necessary for analysis. At present, aldehyde analysis methods are inadequate for reliable analysis of exhaust gases.

Other oxygenates (ketones, ethers, acids, etc.) are currently (if at all) examined through GLC. No specific methods have been employed for them yet.

II. E PRACTICAL USE CONSIDERATIONS

II. E-1 BLEND VOLATILITY CHARACTERISTICS AND EFFECTS

Volatility is loosely defined as the tendency of a liquid to evaporate (87). As discussed in Reference 196, volatility affects engine performance through its influence on the amount of fuel that will change to vapor in manifolds and in cylinders prior to and during the combustion process. In the normal type of spark-ignition engine, operation will be satisfactory only if the various cylinders receive approximately the same fuel-air ratio and if nearly all the fuel is evaporated before ignition. With a given engine at a given set of running conditions, there is a certain minimum volatility below which operation will be unsatisfactory. Conversely, the volatility of the available fuels influences engine design, particularly in regard to the size and shape of the inlet manifold required for satisfactory operation (87). Thus, the volatility characteristics of an automotive fuel are of prime importance. The fuel is used in a great variety of engines which are subjected to large variations in operating and atmospheric conditions. These variations impose many limitations on the volatility of a fuel if it is to give satisfactory performance. Fuels that vaporize too readily in pumps,fuel lines, and carburetors will cause decreased fuel flow to the engine, resulting in rough operation or stoppage (vapor lock). Conversely, gasolines that do not vaporize readily enough may cause hard starting and poor warm-up, acceleration, and distribution (196). Fuel volatility is also found to affect exhaust emissions (132a). The volatility characteristics of automotive fuels therefore must be carefully balanced to provide the optimum compromise of the aforementioned features and must be adjusted to compensate for seasonal and geographic variations in atmospheric temperature and pressure. In this section, the effects of alcohol addition on gasoline's volatility characteristics and their subsequent influence on vehicle performance and emission characteristics are discussed.

DISTILLATION CURVE. The relative volatility of a fuel is ordinarily measured by means of the ASTM distillation test (87). Early studies show that the addition of ethanol to gasoline has a marked effect on the ASTM distillation curve [see Appendix E outline of (32)]. Typical distillation curves for gasoline and ethanol-gasoline blends are illustrated in Figures 21 a and b. Similar data for methanol blends are shown in Figures 22 a, b and c. The distillation curve would be a horizontal line located at 172°F for pure ethanol and at 148°F for pure methanol, which corresponds to the respective boiling points of ethanol and methanol at amospheric pressure. The precise shape of the distillation curve will change from gasoline to gasoline, depending on the relative amounts of the heavy and light fuel components.

When alcohol is added to gasoline, a depression of the distillation curve from the 10% to the 100% point is generally observed. The depression is not the same for the entire curve, however; instead, it is quite pronounced from the 10% to the X% point, the X% point being a function of the alcohol blend level. The greater the alcohol concentration, the larger will be the value of X. For values greater than the X% evaporated point, the depression is small. This characteristic of the blends is illustrated in Figures 21 and 23.

The initial boiling point can either increase, decrease or remain the same when alcohol is added to gasoline. This effect is illustrated in Figure 22 where the initial point is seen to remain the same in Figure 22 a, decrease in Figure 22 b and increase in Figure 22 c.

REID VAPOR PRESSURE. Another measure of a fuel's volatility is the Reid Vapor Pressure (RVP), which is the equilibrium pressure measured at 100°F in a container initially having a four to one volume ratio of air to liquid fuel (196). The effect of alcohol addition on a gasoline's RVP has been reported for both ethanol (viz. 29, 31, 32, 76) and methanol (viz. 161, 171, 188).

Data in one of the earlier References (32) show a rather rapid increase in RVP with the addition of small amounts of ethanol, reaching a maximum value at around 8%E with a subsequent decrease to the RVP value for the base gasoline at around 30%E; a lower-than-base gasoline RVP follows at higher ethanol concentrations (see Figure 23a). The more recent data of Reference 187 for methanol blends are also included in Figure 23. Figure 24 shows that the rate of change of the RVP with ethanol addition is a function of the base gasoline's composition. For some gasolines the RVP is found to increase while for others it is found to decrease with ethanol addition.

The effect of methanol addition on RVP is more pronounced than that observed for ethanol addition. While ethanol blend data show maximum increases in RVP in the order of 1 psi or less over that of the base gasoline, the limited methanol data available show larger increases. The data of Wigg and Lunt (187) show 2.4, 4.1 and 2.1 psi increases in RVP when 15% methanol blends were formed with gasolines having intially 10.4, 11.9 and 13.6 psi RVP respectively. They also show that, similar to the trends observed with ethanol blends, the RVP of methanol blends increases very rapidly for small blend levels. This is illustrated in Figure 23 b. The increase reaches about 3 psi at 2%M and then rises slowly to approximately a 2.5 psi increase at around 8%M. Hurn and Chamberlaine (189) report similar results; the RVP of a 12 psi gasoline rose by about 2 to 2.5 psi on forming a 10%M blend. From the limited data available it is concluded that a 2 to 4 psi increase in RVP can be expected for methanol blend levels of around 5 to 15%.

It has been pointed out that if blends are to be used in vehicles having the same vapor locking tendencies as today's automobiles, it will be necessary to back out of the base gasoline some of the lighter boiling fractions such as butane to maintain an acceptable RVP. This in turn would decrease the approximately Y% increase in the energy content of the gasoline pool which could accrue from using 2Y%N blends. It has also been pointed out that the shale and coal-derived fuels with their higher-than-conventional-gasolines aromatic content will probably require the blending in of some low-boiling point, non-aromatic fractions (190). This potentially could create a use in the gasoline pool for those low-boiling fractions that would be removed from the conventional base gasoline blending stocks used to make methanol blends. Another automotive use for the removed light-fractions is as an ingredient for 100%M-fueled engine operation. Jackson and Tillman (171) report the RVP for pure methanol to be 3 psi. They increased the RVP to acceptable levels by blending with butane; a 90%M, 10% butane blend had an RVP of 12 psi. It is apparent that a comprehensive assessment of the effect of methanol on the gasoline pool's energy content will have to take into account all of the considerations given above.

COLD START. The importance of any point on an ASTM distillation curve depends on the temperature range in question. Under low-temperature conditions, as in cold weather starting when only a small portion of the fuel is evaporated, the low-temperature end of the curve is of chief importance (87). The ASTM 10% point has been generally accepted as a good indication of the relative starting ability of full-boiling range gasolines (87, 114). Other investigators (81a) have used the percent evaporated at 158°F as a parameter to correlate cold start data. The lower the 10% point temperature or the greater the percent evaporated at 158°F, the more readily will the engine start at colder temperatures.

10% Point Correlation: As discussed above under "Distillation Curve," the effect of alcohol addition on the shape of the distillation curve depends on the base gasoline as well as on the alcohol blend level. Bridgeman (29) presents 10% point temperature data for a number of different gasolines with 10%E. When the ethanol was added to gasolines of low 10% point temperatures, the alcohol raised the temperature for the 10% evaporation point. Conversely, when ethanol was added to high 10% point temperature gasolines, the 10% point temperature was lowered. He points out that insufficient work has been done with blends containing various percentages of alcohol to make possible any general formulation of a relation between their distillation characteristics and engine starting. Bridgeman presents experimental results, however, which suggest that the 10% distillation point can also be used for correlating 10%E blend starting data. The results are presented in Figure 25, which is taken from Tables IV and V in Reference 29 . It is not clear from Bridgeman's paper how many of the points in Figure 25 are actual data points and how many are extrapolated, for he mentions that testing was not done at the "low" ("low" is not defined) temperature values. At the "higher" temperature levels, however, there is a correlation between the 10% point and minimum starting temperatures for both gasoline and gasoline-10%E blends. The data shows that the acceptable starting temperatures for the ethanol blends are somewhat higher than those for gasoline even at the same 10% point temperature. The difference is small, though, being less than 3°F.

Little data are available regarding the effect of methanol addition on the 10% point temperature. Wigg and Lunt's results (187) show a 5 to 12°F drop in the 10% point temperature when 15% methanol blends were formed with various gasolines. Assuming that the 10% point temperature can be used to predict ease of starting, these results indicate easier cold starting with the blends; however, when the vapor lock index (VLI) was adjusted to the same value as the base gasoline, a condition necessary to avoiding vapor locking problems as discussed later the 10% point temperature was found to increase between 6 and 10°F, indicating more difficult cold starting.

Rogers (144) presents data showing substantially larger decreases in the 10% point temperature for 5 and 10%M blends formed with regular and premium base stocks. The decreases were between 19 and 26°F.

Percent Evaporated at 158°F Correlation: Moore et al. (81a) present cold-start data relating starting time to the percent evaporated at 158°F for 1956 vehicles with V-8 engines. For low temperatures, 0°F and -20°F, there was a definite decrease in the engine cranking time required for first firing as the percent evaporated at 158°F increased. For higher temperatures, 20°F and 40°F, the percent evaporated at 158°F had no effect on the starting time which was below one second for the fuels tested. The distillation curves illustrated in Figures 21 and 22 show that there is a definite increase in the percent evaporated at 158°F for alcohol blends even when the VLI is adjusted to the same value as the base gasoline. This would indicate easier starting with alcohol blends. It has not been demonstrated, however, that the percent evaporated at 158°F can be used to corralate methanol blend start-up data.

Data: The limited data regarding cold start tests with methanol-gasoline blends is favorable. Reed (176) used a 10%M blend in a 1969 Toyota throughout most of the winter in Boston, Massachusetts, and it seemed to give improved starting.

At the present, there is too little information available to make firm conclusions. However, the above considerations indicate that cold starting, as it is affected by fuel volatility, will probably be improved if methanol is added to gasoline.

WARM-UP. For gasoline the 50% evaporated temperature is a broad indicator of engine warm-up under cold starting conditions (196). The 90% evaporated temperature, if varied over a range of 100°F, is also found to affect warm-up, though the effect is of considerably less importance than that of the 50% evaporated temperature (81a). The 20% evaporated temperature has also been found to correlate with warm-up data for gasolines having similar high range volatility as discussed in (87).

Warm-up tests show that in general the warm-up performance is improved as the 50% (or 20% or 90%) temperature is lowered for gasoline. If the same type of correlation is found for methanol blends, then the limited distillation data available (Figure 22) suggests that warm-up performance, as it is affected by volatility alone (ignoring the influence of increased latent heat of vaporization), will be improved if methanol is added to a gasoline without any adjustment of the VLI or RVP.

Based on the following observations it is suspected that methanol blends may not follow the same correlations found for gasoline:

1. Moore et al (81a) have shown that a fuel having a low 50% (and 20%) evaporated temperature gives very poor performance during warm-up. The fuel used was unusual in that it had a sharp rise in temperature from the 40% point to the 60% point. They concluded that the high 60% portion of the distillation curve caused the poor warm-up performance.

2. Wigg et al. adjusted their 15%M blend to have the same RVP (Figure 22b) as the base fuel in one case or the same VLI (Figure 22c) as the base fuel in another case, they also found a sharp increase in temperature between the 40% point and 60% point. While the increase was not as large as t that found by Moore et al.,.it was to a temperature above that of the base gasoline, thus indicating the potential for poor warm-up performance. In addition, the matched VLI fuel of Figure 22c had a higher 50% poin than the base fuel, and the matched RVP fuel of Figure 22b has a higher 20% point.

3. Ungelman et al., as discussed in (130), concluded that "while the 50% evaporated temperature is used in most cases, a slightly higher distillation point may be more effective (in correlating warm-up)," and that "the 90% point is more significant than the 10% point." This statement, along with the distillation curves shown in Figure 23, further enhances the concern for potential warm-up problems with matched-to-gasoline RVP or VLI methanol blends.

4. To the above items must be added the effects detrimental to warm-up of the higher blend latent heat of vaporization.

The limited warm-up data found was that of Jackson (100). Using a 25% (wt) ethyl alcohol blend he experienced warm-up problems with two 1964 vehicles and none with a third 1964 vehicle.

From the limited data available and from the considerations given in previous paragraphs, it appears that warm-up problems may be experienced with methanol blends as a result of the change in the distillation curve as compared to that of the base gasoline when the blend is adjusted to give equal-to-gasoline RVP or VLI.

WARM-ENGINE PERFORMANCE. Engines are designed to operate satisfactorily, when warm, on a fuel of certain minimum volatility. When a fuel of this minimum volatility is used in a warm engine, inlet-air and manifold temperatures along with inlet system and fuel-system design, are such as to give good distribution and sufficient vaporization in the intake manifold with the normal range of fuel-air ratios (87). The degree of vaporization is therefore determined by the manifold design as well as by the volatility characteristics and latent heat of vaporization of the fuel.

For gasoline, the optimum degree of vaporization in the intake manifold is around 60% (114). As pointed out by Adelman et al. (128), for methanol the situation may be quite different. The optimum degree of vaporization could also be different for methanol blends. In order to determine a first order estimate of the intake manifold design temperature for neat methanol, Adelman et al. assumed the usual 60% evaporation in the intake manifold.

Their results show the design temperature for methanol to be essentially the same as that for gasoline. For the blend levels anticipated, the optimum degree of vaporization for the blends will probably be close to the 60% value for gasoline. This, in conjunction with Adelman et al.'s calculations (128), indicates that optimum manifold design temperatures for the blends will be close to that of gasoline. Hence, the potential deficiency in the gasoline engine's intake manifold design when it is used for blends will be that of its heat transfer area, which ideally should be increased to compensate for the increase in the blend's latent heat of vaporization as discussed in section II. A-3. The increase might be less than that found only from latent heat of vaporization if the optimum degree of vaporization for the blends is less than 60%.

In order to determine more quantitatively the best manifold design temperature and heat transfer area, it will be necessary to determine experimentally the optimum degree of vaporization in the manifold and equilibrium air distillation (EAD) curves for methanol-gasoline blends.

Wigg and Lunt (187) made an interesting observation during the testing of 15%M. In a 1967 normally rich-operating vehicle, they found that the high volatility of this fuel apparently led to carburetor enrichment during warmed-up operation which counterbalanced the blend-leaning effect. This phenomena, however, was not observed in a 1973 lean-operating vehicle slightly richer-operating 1973 vehicle equipped with a catalyst.

HOT START. When a warm engine is idled or shut down (i.e., hot soaked) after a moderate- or high-powered run,the fuel system temperatures are found to increase substantially over the steady state values found during the run. Some data show the temperature to increase from a value of around 120°F during the run to 180°F in the carburetor bowl and 190°F at the main fuel jet (114). These temperature levels will of course depend on engine and vehicle overall design configuration and environmental temperature, but the trends observed show that there can be vaporization of the lighter fractions in the float chambers and fuel passages in the carburetor during the hot soak period. Unless precautions are taken, fuel vapor can flow from the float chamber into the intake manifold [internal venting (130)]. If the venting is restricted, the float chamber pressure can increase,causing fuel to be forced through the main carburetor jet into the intake manifold [percolation (130)]. Internal venting and percolation result in a rich mixture in the intake manifold which then causes increased starting difficulty and can increase hot start HC emissions.

Figures 22 a-c show that when methanol is added to gasoline,there is a rather large increase in the amount of fuel constituents capable of being evaporated at the temperature levels attained in the carburetor during a warm soak. The above considerations indicate that hot start problems will probably be more severe for the blends than for the base gasline. Difficult hot starting and rough hot idle were, however, only of low frequency in Wigg and Lunt's fleet tests (187). Difficulties observed were more vehicle age-related than fuel-related. An understanding of methanol blend hot start characteristics requires further study.

VAPOR LOCK. Vapor lock is defined as a serious restriction of the fuel supply due to excessibely rapid formation of vapor in the fuel system or carburetor (87). Such a reduction in the fuel flow can cause a loss in power or complete engine stoppage. A number of indices are used to measure the relative vapor locking tendencies of gasolines including the RVP, the vapor lock index [VLI (187); also termed the front-end volatility index (114)] and the vapor liquid ratio [V/L (87)]. Other indices are discussed in (114).

Wigg and Lunt's (187) results indicate that the VLI, as defined by

$$VLI = RVP + 0.13\% \text{ distilled @ } 70^{o}C\ (158^{o}F)$$

can also be used as a measure of the vapor locking tendency of 15%M blends. The data presented by Bridgeman (29) indicate that for the same freedom from vapor lock, the RVP of a 10%E blend should be about 1 psi lower than that considered permissible for gasoline. Similarly, Wigg and Lunt (187) found a greater vapor locking tendency for 15%M blends than for gasolines having the same RVP. It thus appears that the RVP and VLI tendencies for gasolines can also be used as indicators of the relative vapor locking tendencies for blends with the exception of a slight modification when using the RVP.

When alcohol is added to gasoline the vapor locking indices RVP, VLI and V/L all change to values corresponding to a greater vapor locking tendency. The RVP is found to rapidly increase as alcohol is added to a maximum value and then to decrease for higher alcohol levels (Figure 23). Wigg and Lunt (187) have found the VLI to increase for 15% blends. This, of course, follows from the above equation defining VLI as the sum of the RVP and 0.13 times the percent distilled at $158^{o}F\ (70^{o}C)$, both of which increase as methanol is added to gasoline. Taliaferro reports that at values of

V/L of "20 or 30 to 1, ratios at which car-fuel systems encounter vapor lock, the temperatures for the blend are four to five degrees lower than those for the gasoline, indicating that the blend would encounter incipient vapor lock at four to five degrees lower ambient temperatures than the gasoline (104)."

Experiments are in agreement with the above considerations. Wigg and Lunt found a marked increase in vapor locking tendency when no front-end volatility adjustments were made to a 15%M blend (187).

It thus appears that there will have to be modifications made to the base gasoline when methanol is added if the same degree of freedom from vapor lock is required.

EMISSIONS. Fuel volatility per se has been reported to affect emissions in two ways: 1) Clarke (132a) reports that volatility affects cylinder-to-cylinder distribution which in turn affects CO emissions and to a lesser extent HC emissions; 2) Wigg and Lunt report that the high front end volatility of non-RVP matched-to-gasoline methanol blends is suspected of causing carburetor enrichment for some vehicles with a subsequent increase in CO emissions. These two effects are discussed below.

1) When comparing fuels composed of hydrocarbon compounds, Clarke (132a) found the VLI to be a good overall parameter for correlating emissions and fuel volatility. A larger VLI results in more fuel vaporization in the intake manifold, which in turn leads to better distribution and lower emissions. For the fuels tested ($6.6 < \text{RVP} < 14.8$ psi) an increase in the VLI of 7.5 units, which corresponds to an increase of approximately

5 psi RVP, decreased the CO levels an average of 28% at 70°F (21°C). The decrease was about 22% at 30°F (-1°C). The corresponding decrease in HC emissions was about 5% at 70°F and 6% at 30°F.

The emissions versus VLI correlations found for the hydrocarbon fuels are not expected to be directly applicable for methanol blends. Volatility consideration alone would indicate lower CO and HC emissions, since the VLI of a methanol blend is greater than that of the base gasoline. The greater latent heat of the blend, however, would indicate the opposite effect. A second factor making the VLI emissions correlations not directly applicable is the blend-leaning effect, because the effects of maldistribution on emissions are a function of the operating point equivalence ratio. In the region where the CO and HC emissions versus equivalence ratio curve is fairly steep and non-linear, the effects are most important. The blend-leaning effect can shift the operating point to a location where the effects of maldistribution on emissions are different from those for the base gasoline. An additional factor affecting the applicability of the correlation are the plateaus in the methanol blend ASTM distillation curves which were absent for Clarke's fuels.

2) As discussed under "Warm-Engine Performance," the high front end volatility of methanol blends is suspected of causing carburetor enrichment for some vehicles during warmed-up operation. The degree of enrichment was found to be sufficiently large to partially nullify the CO reduction attributable to the blend-leaning effect in a 1967 rich-operating vehicle.

It thus appears that the effect of blend volatility per se on exhaust emissions is rather complex; further research is needed for a complete understanding.

II. E-2 BLEND SOLUBILITY AND WATER TOLERANCE

In general, the solubility of alcohol in gasoline is a function of the gasoline hydrocarbon make-up, the temperature and the water content. The detailed solubility characteristics of methyl and ethyl alcohol, however, are quite different (122). For example, dry ethanol is reported to be miscible in all but a very few gasolines (15, 122). Dry methanol, on the other hand, is miscible in all proportions in only a very few fuels. Because of their differences, only methanol is discussed below.

When comparing hydrocarbons of the same boiling point, dry methanol is least soluble in saturated hydrocarbons, intermediate in olefins and naphthenes, and most soluble in aromatics (173). Because of this, dry methanol will be found to have different degrees of solubility in different gasolines. For example, it has been found to be miscible in all proportions in an aromatic gasoline at 60°F, miscible up to 13% in regular gasoline, and only up to 4% in an all-straight run gasoline (122). Table 7 contains data on the solubility of methanol in various gasolines along with the composition of the gasoline as taken from (144).

As discussed by White et al. (173), temperature is found to have an influence on the amount of methanol that can be dissolved in a saturated hydrocarbon. As a result, some commercial gasolines will not maintain more than 4 or 5%M in solution during low temperature, winter-time operation even under perfectly dry conditions (173).

Water is found to have a strong effect on the solubility of methanol in gasoline. While methanol is soluble in gasoline containing normal (25-35 Vol.%) amounts of aromatics, separation into a two phase system occurs if small amounts of water are introduced (134). The water tolerance is greater for higher %M blend levels as is discussed below.

There are additives which increase the tolerance to water of methanol blends. Typical additives are the higher alcohols (122, 134, 144, 170, 173, 187). The influence of water and additives on a methanol-gasoline blend are typified in the Gibbs triangle of Figure 26, which is taken from (176). The methyl fuel referred to is a mixture of methanol and higher alcohols (195). The bottom left hand point, labeled point G, represents 100% gasoline. Points along the axis connecting points G and M represent mixtures of methanol (or methyl fuel) and gasoline with zero water content, point M representing 100% methanol (or methyl fuel). A mixture of gasoline and water is represented by a point on the horizontal line connecting the points labeled G and W with point W representing 100% water. Similarly, mixtures of methanol (or methyl fuel) and water are represented by points along lines M-W. Mixtures of gasoline, methanol (or methyl fuel) and water are represented by points within the area bounded by the lines connecting points G, M and W. Points along the line D-W represent mixtures formed by initially blending 20 volume percent methanol with 80 volume percent gasoline (point D) and then adding water to the mixture. The point E, for example, represents a mixture containing 70% gasoline, 17.2% methanol and 12.8% water.

The curve labeled Methanol separates the methanol-gasoline-water mixtures which will be found in a single phase from those which will separate into two phases. As indicated in the figure, mixtures represented by points below this curve will separate into two phases; those above will remain homogeneous. Similarly, the dashed curve labeled Methyl Fuel separates mixtures of methyl fuel, water and gasoline, which remain homogeneous from those which will separate into two phases.

Methanol for the particular gasoline represented in Figure 26 is soluble at all blend levels up to 100%M, provided the water content is zero (Line A-B). The introduction of small amounts of water, especially at low %M blend levels, result in separation into two phases. According to (176), for zero percent methanol, the solubility of water in the gasoline is about 0.01% (1 gallon water in 10,000 gallons gasoline). For a 10%M blend the water solubility limit is raised to 0.1% (10 gallons water in 10,000 gallons of blend). The addition of blending agents in the form of the higher alcohols, as is found in the methyl fuel, results in a somewhat greater tolerance for water before the two-phase region is entered. For a 10% Methyl fuel blend the water solubility limit is 1% (100 gallons water in 10,000 gallons of blend). This greater tolerance, however, is not considered sufficient for all applications. Ingamells and Lindquist (170) examined over 150 water solubilizing additives and could find none that were sufficiently effective in preventing phase separation at reasonable additive concentrations.

Suppliers of petroleum products are in general agreement that the inability of methanol to remain in solution in the presence of the water found to be present in gasoline storage and distribution systems will require extensive changes in fuel handling equipment and operating procedures (137, 170, 173, 187) and that this inability is probably the most critical product quality factor associated with the use of methanol blends.

Separate fuel distribution systems would probably be required (170). There would then be the need to protect the hygroscopic methanol blends from the atmospheric water content when blends are stored in the vehicle's fuel tank.

II. E-3 MATERIALS COMPATIBILITY

One of the most important considerations to be determined on the practical aspects of using methanol or methanol-gasoline blends as an automotive fuel is the compatibility of methanol with the materials in the fuel system in existing automobiles. Today's automobile fuel systems have been developed by evolution, using materials which are fully compatible with th current composition of gasoline. Very little information is available on the corrosion problems of fuel systems. Most of the information available on automobile corrosion (107, 112) is related to body and external corrosion.

The chemical properties of methanol and gasoline are quite dissimilar and thus could be expected to react differently with different materials. Corrosive rates of several materials are given below.

Corrosion Rates of Materials in Methanol at 75°F
(From Perry's Chemical Engineering Handbook
McGraw-Hill 1963) Page 23-25

Aluminum	< 0.005 inches/year
Copper Bronze	< 0.02 inches/year
Cast Iron	< 0.02 inches/year
Lead	< 0.02 inches/year
Steel	< 0.02 inches/year
Stainless Steel	< 0.002 inches/year .02 - .05 at 250°F
Epoxy Resin	No Attack
Polyethylene	Some Attack
Polyvinyl Chloride	Some Attack

Perry's Chemical Engineering Handbook
McGraw-Hill 1963 Page 23-12

Chemical Resistance of Plastics

Polypropylene	Gasoline - Poor Alcohol - Poor
Polyethylene	Gasoline - Poor Alcohol - Poor
Cellulose Acetate Butyrate	Gasoline - Excellent Alcohol - Poor
Polyvinyl Chloride	Gasoline - Excellent Alcohol - Excellent

A major difference in physical properties of methanol and gasoline is that water is completely soluble in methanol and methanol will absorb water. Water is insoluble in gasoline and gasoline will absorb only a trace amount (173). When a blend of alcohol and gasoline has water added, the blend will separate into two phases. The limits of the single and two-phase liquid are shown in Reference (122). The addition of water changes the corrosive rates of methanol. Parker (111) points out that the corrosion rate of mild steel in methanol is 0.002 inches per year while methanol-10% water has a corrosive rate of 0.020 inches per year. Kant (190) suggests that possible corrosion in the fuel system is a serious problem with methanol-gasoline blends.

Pleeth (67) points out that some of the early cars had fuel tanks which were internally lacquered. While this was satisfactory with gasoline, the addition of alcohol stripped the lacquer or shellac from the tank. He states that fuel pump diaphragms of normal rubber (used in earlier cars) will disintegrate on contact with alcohol blends, but new synthetic rubber is satisfactory. He did not believe that wear with alcohol was any problem.

The standard material for recent and current automobile fuel tanks is Terne plate (153). Terne plate is used because it is corrosion-resistant, readily soldered and welded, and can be easily drawn to produce economical, leakproof tanks. U.S. Steel (81) describes terne plate or terne-coated steel as low carbon steel coated by immersion in a bath of terne metal (10% to 20% tin with the balance lead).

Carburetors have traditionally been die cast from zinc or zinc alloys (182). Due to the demands of higher operating temperatures, some manufacturers are moving toward aluminum for certain applications in the carburetor. Most carburetors use brass for metering jets and most other fittings.

In an early study of ethanol gasoline as a fuel, Egloff (32) reported that there were problems with hoses, pump diaphragms, and tank coatings and that water in blends caused corrosion. He also reported greater wear in an engine when alcohol was used. Christiansen (31) reported that with the exception of tin, there was less corrosion by alcohol on metals than by gasoline. He stated that both ethanol and methanol reacted with magnesium and aluminum at elevated temperatures.

In a recent study Ingamells and Lindquist (170) report that the methanol-gasoline blend results in corrosion of the fuel tank. The blend attacks the coating of the terne plate, forming lead hydroxide which can plug the fuel filters and carburetor. Subsequent corrosion of the underlying steel results in rusting of the fuel tank. In cars equipped with an electric fuel pump, they observed extremely rapid corrosion of the fuel system. They point out that magnesium and magnesium alloys are very susceptible to corrosion by gasoline methanol blends. In a study of the reaction between elastomers in the typical automobile fuel system they found three material problems:

1. methacrylate plastic expanded and softened
2. viton tips used on carburetor float valves swelled

3. fiber gaskets softened.

They conclude that, for satisfactory use of methanol-gasoline blends, vehicle fuel systems must be constructed of methanol-resistant materials or component failure will result.

To evaluate the storage problem of methanol-gasoline blends Texaco (134) evaluated several storage and automobile materials. They found that copper corroded twice as much in gasoline-20% methanol as in gasoline, while brass corroded about the same in each. Steel, terne metal and carburetors corroded much less in the blend than in the base fuel.

Rogers (144) noted that there was no corrosion of automotive parts in gasoline-alcohol blends in a sealed (dry) system. In vented systems "wet" with condensed moisture, he found increased corrosion rates in aluminum, iron, and galvanized iron.

Several investigators (125 , 176) have operated automobiles and automobile engines on methanol-gasoline blends and have not reported any serious corrosion or materials-compatibility problems.

The materials used in automotive fuel systems are generally metal; however, several new materials have been reported. Fuel tanks fabricated from high density polyethylene resins have been used in a limited number of trucks and light vehicles (106 , 108). Nylon fuel tanks have been offered as optional equipment on some vehicles. In addition, fuel tanks made from aluminum (153) have been described.

Other new fuel system materials include aluminum carburetor parts and plastic components in the carburetor (172).

II. E-4 ENGINE WEAR

Several studies described above have noted an increase in engine wear with the use of methanol-gasoline blends. Pleeth (61) reported a 50% increase in wear rate with an ethanol blend in a truck fleet in England compared with regular gasoline. A more recent study (144) concludes that wear is likely to be no greater with ethanol blends than with commercial gasoline. Using 100% methanol as a fuel as well as using a very high quality lubricating oil during Sequence V-C oil rating tests, Tillman (180) observed excessive wear of the soft piston rings specified for the test and a corresponding excessive oil consumption rate. The test was run again with standard rings. Excessive oil consumption was observed again about half-way through the test. This time the cylinder walls were found to exhibit excessive wear. He also observed excessive valve guide wear in a 100% methanol-fueled Pinto engine. The wear appeared to be correlated to rich air-fuel ratio operation. As pointed out by Tillman these results show that wear problems can occur if 100% methanol is used as a fuel without the addition of upper cylinder lubricants as are normally used in racing applications.

III. SUMMARY

III. - A NEAT METHANOL

The survey presented in Section II shows that improved energy conversion efficiency, improved power output, and reduced emissions except for aldehydes will be found with methanol-fueled engine operation as compared to gasoline-fueled engine operation. In fact, neat methanol is found to be very favorable with respect to meeting the Federal Emissions Standards (Table 6).

It is not clear in all cases exactly why the observed improvements in performance and emissions do occur. It is generally accepted, however, that the fuel property which has the greatest influence is the latent heat of vaporization, which is much greater for methanol than for gasoline. Potentially positive effects of the high latent heat have been identified. These include increased volumetric efficiency, lower compression stroke work and lower Otto cycle temperatures. On the negative side, the high latent heat can increase cylinder-to-cylinder maldistribution. There are other fuel characteristics which have also been identified as influencing performance and emissions. Dissociation during the compression stroke with subsequent reduction in compression temperature is one of them. The observed increase in flame speed should be related to the compression stroke dissociation, which would also affect ignition delay. No data or calculations regarding compression stroke dissociation were found, however.

Equilibrium and chemical kinetic calculations show CO and NO_x production to be lower than that from gasoline combustion even at equal equivalence ratios. These tendencies are confirmed by experiment except for some data at higher loads where NO_x emissions appear to be the same for methanol and gasoline. Methanol-fueled engine NO_x emissions, in contrast to the gasoline case, are found to contain substantial amounts of NO_2.

Total HC emissions (including methanol) are also found to be lower than those from gasoline-fueled engines provided there is proper warm-up and fuel preparation in the intake manifold. The compounds in the exhaust containing hydrogen and carbon are found to be mainly methanol and formaldehyde. The formaldehyde emissions are greater than those from the gasoline case.

Polynuclear aromatics, including the carcinogens, appear to be at least one order of magnitude lower than those from the gasoline-fueled counterpart.

In addition to the above effects, methanol, as a result of its relatively high flame speed at lean mixtures, can be operated efficiently at less than gasoline equivalence ratios. This fact has been used to substantially reduce emissions of CO, NO_x and total HC.

Methanol has a very high Research Octane number. Its sensitivity, however, is greater than that of gasoline and its Motor Octane number increase over that of gasoline is not as great as the increase found for the Research Octane number. Road Octane characteristics of methanol have not as yet been determined.

A significant disadvantage of methanol as a vehicle fuel is its low volumetric and gravimetric heating value. This will result in an approximately 50% greater volume-and-mass fuel consumption.

Another problem encountered with methanol as an automotive fuel is start-up. For operation at ambient temperature below around 77°F it will be necessary to blend in various low boiling point hydrocarbons which may be in short supply.

III - B METHANOL-GASOLINE BLENDS

General agreement was found in Section II that the blend-leaning effect is a major factor in causing the observed change in the performance and emissions when 20 to 25% or less methanol blends are substituted into an unmodified vehicle. The influence of the blend-leaning effect per se on performance and CO, NO_x and total HC emissions is found to be a function of the blend stoichiometry used for gasoline operation as well as of the blend level. Figures 4 through 7 and 12 through 17 illustrate graphically these functions.

The blend leaning has also been shown to cause driveability problems in some late model vehicles which operate lean on gasoline. This is especially true for vehicles having marginally acceptable driveability with gasoline.

The substitution of a methanol blend, in addition to resulting in an effectively leaner mixture, also changes the fuel's volatility characteristics. The increased front-end volatility can lead to vapor lock problems. It can also cause the hydrocarbon emissions from a warmed-up engine to be greater than those from blends with matched-to-gasoline front-end volatility. It appears to be necessary to remove from the base gasoline some low-boiling-point hydrocarbons if blends are to be used in vehicles having the same vapor locking tendencies as the current gasoline-fueled vehicles.

The influence of methanol addition to gasoline on organic compound emissions is not clear; conflicting data are reported. The influence is found to be a function of the stoichiometry used for gasoline operation and of the blend RVP. It does appear, however, that there is a definite increase in aldehyde emissions. The dominant aldehyde species is formaldehyde. Methanol is also found in the exhaust. The methanol levels are reported to be about the same as that of the formaldehyde. It is also found that there are significant reductions in polynuclear aromatics including the carcinogens.

Methanol addition is found to affect Research Octane numbers and to a lesser extent Motor Octane numbers. The limited data available sho it to have a small influence on the road rating of a premium gasoline.

With regard to practical use, methanol blends are found to exhibit strong tendencies to separate when a small quantity of water is present.

III.-C EMISSIONS MEASUREMENTS

It can be seen from Section D that standard acceptable methods are available for a number of the prominent emission products,viz. CO, CO_2, NO, NO_2 and total (excluding oxygenates) HC. At the same time, there do not appear to be proven methods of analysis for such compounds as the oxygenates.

In Table 7 various emission species are summarized along with acceptable methods used for measuring their concentration in the exhaust gas. The Table is divided into two groups. The first group contains methods which yield continuous real-time measurements; this type of measurement is generally preferred over the discontinuous type of measurement made with the methods listed in the second group. Also included in the Table are a few of the potential methods that might be developed for determination of some of the listed exhaust gas species.

Other potential methods which are not mentioned in the Table include micro-wave spectroscopy and Fourier-transform. An adaption of older methods such as gas density, ultrasonic, flame photometric, electrochemical and catalytic ionization detectors could also be included as potential methods of analysis.

With the standardized and acceptable techniques three problems have been identified. The first is the reduced response of the FID to the oxygenated hydrocarbons found in methanol-fueled and methanol-gasoline-fueled engine exhaust. The second is the loss of methanol in exhaust gas water condenser traps that are usually employed with unheated FID's and raw (undiluted) exhaust sampling systems. The third problem is that such traps can also remove, along with the water, some of the substantial amounts of NO_2 found in methanol-fueled engine exhaust.

III. D MATERIALS COMPATIBILITY

The survey shows no definite trends for the compatibility of automotive materials with methanol and methanol-gasoline blends. Several reports (134, 170, 171) indicate corrosion or materials deterioration when in contact with methanol-gasoline blends, but the results are not conclusive. For example, the Ingamells and Lindquist report indicates severe attack by the fuel mixture on the terne plate used in vehicle fuel tanks (170), while Texaco (134) reports less corrosion of the terne plate by a 20% methanol blend than by base fuel. In addition, several investigations have been running vehicles on a fuel mixture without reporting any corrosion problems.

Several cases of problems with plastic parts have been reported when alcohol fuel is used, such as swelling of plastic carburetor float, plastic fuel filters, plastic carburetor float valves, and fiber gaskets.

One of the causes of the inconsistent results may be the water sensitivity of the methanol-gasoline mixture. Materials may react differently in methanol-gasoline mixtures than in methanol-gasoline-water mixtures. There have been no reports of studies concerned with these different mixtures and their respective reactions with various materials.

The reports of engine wear are also inconsistent. Both increased wear and n effect have been observed when methanol-gasoline blends are used.

While no definite trends have been found, the survey shows that when methanol or methanol-gasoline blends are used in unmodified vehicles, materials compatibility can be a significant problem.

IV. CONCLUSIONS AND RECOMMENDATIONS

IV - A. NEAT METHANOL

Neat methanol appears to be an attractive fuel for automotive applications. The potential improvements in performance and emissions characteristics for methanol-fueled operation, however, have not been fully exploited in multicylinder engines. Tests to date have been made with engines originally designed to operate on gasoline fuel and modified to give reasonable performance with methanol.

Contrary to the methanol-blend scenario of unmodified engines, the neat-methanol scenario would involve its use in captive fleets of vehicles housing modified engines. Such a use, coupled with the potential improvements in performance and emissions characteristics, warrants more extensive engine modifications than have been made in past studies. Topics requiring further research and understanding if engines are to be optimized for neat methanol fuel are described in the following paragraphs.

Fuel preparation is perhaps one of the most important engine functions requiring further study. Fast warm-up manifolds giving even fuel distribution are required. The inability of conventional manifolding to perform this function satisfactorily for methanol has been reported by all investigators who have used it as a fuel. In connection with this, carburetors can probably be optimized for methanol to give better atomization. Improvements along these lines have already been made (158).

In the light of methanol's ability to operate satisfactorily at leaner-than-gasoline equivalence ratios, the optimum metering characteristic of a methanol-fueled engine carburetor will be different from its gasoline counterpart. Studies should be carried out to determine carburetor characteristics which will give a satisfactory trade-off between performance and emissions over a wide range of operating conditions.

Since methanol has a higher flame speed, optimum ignition timing will, in all likelihood, be different from that for gasoline and should be determined. In connection with this, fundamental studies should be carried out which measure both flame speed and ignition delay. Research is also needed to optimize ignition system voltage characteristics and spark plug selection.

Because of methanol's high octane number, compression ratios can probably be raised to increase efficiency. The amount the compression ratio could be raised will depend on the Road Octane rating. Increased compression ratios would increase the low NO_x levels found with methanol operation. It might be necessary to counter this increase by employing exhaust gas recirculation (128). This measure could also help improve fuel economy if the hot exhaust gas recirculated into the fuel-air mixture helped vaporize the fuel and thus improve mixture homogeneity (194).

Both compression stroke dissociation and evaporation during the compression stroke have been identified as being beneficial to engine performance. Definitive studies along these lines, however, have not been made. It is of fundamental importance that such studies be carried out.

In the process of developing an optimum methanol-fueled engine consideration will, of course, be given to emission characterization. To date, no research has been described in the open literature, whose goal was to optimize emission control techniques for methanol-fueled engines. Such research is needed.

As described in Section II, the hydrocarbon composition of methanol-fueled engine exhaust gas is different from that of gasoline-fueled engines. Studies should be carried out to ascertain its relative reactivity. Also, the environmental impact of exhaust from captive fleets of methanol-fueled vehicles should be studied.

The effectiveness of evaporative emission control techniques applied to methanol must also be investigated.

In addition to the above-described fundamental and developmental type of research, fleet tests should be conducted to uncover the engine-related practical problems which will arise when neat methanol is used as a fuel, such as cold start, hot start, vapor lock, driveability, engine wear, and lubrication. Fleet testing should be done at various places around the country during different times of the year to ascertain the effect of atmospheric conditions on the results.

It is probable that the synthetically produced methanol fuel of the future will, in fact, be a mixture of methanol and higher alcohols and possibly butane and natural gas liquids rather than pure methanol (195). Research is needed to characterize such a fuel, including synthetic gasolines.

There is a paucity of data concerning the use of methanol as a fuel for engines other than the conventional, carburetted, spark ignition engine. Methanol has been shown to be a good fuel for both the stratified-charge and fuel injection engine. More research is also needed in this area, however, to completely characterize the use of methanol in automotive powerplants expected to be used in the future.

IV - B. METHANOL-GASOLINE BLENDS

In contrast to the neat methanol fuel scenario with captive fleets of vehicles having duly modified engines, the generally accepted methanol blend scenario is that of unmodified vehicles in which either or both gasoline and methanol-gasoline blends will be used as fuel. It is therefore essential to ascertain the changes that occur in performance and emissions characteristics when blends are substituted for gasoline in vehicular powerplant configurations expected to be in use when methanol blends might become available. Such powerplants include those in use today as well as those to be produced in the future.

A number of investigators have reported on the influence of methanol blends on performance and emissions characteristics as discussed in Section II and in the Summary. These reported experiments usually result in data obtained from tests carried out over a driving cycle with carburetted engines. Such data are essential. It is also of importance, however, to know in more detail the changes that occur at particular operating points over a wide range of operation. Such information would help to better understand the causes of the changes in performance and emissions observed over driving cycles. Thus, a systematic study is needed to ascertain in more detail the effects of methanol addition on multicylinder engine performance and emissions characteristics.

There are no blend data presented which are taken in a multicylinder engine with the carburetor, spark advance, and manifold heating adjusted for optimum blend-fueled engine performance. Such information would be of importance for future carburetted engine design considerations should they be expected to utilize both methanol blends and gasoline as fuel. Such engines would not be designed for gasoline as were the ones tested in the past. Rather, the design would be a compromise for dual-fuel (gasoline and gasoline-methanol blends) operation.

No data was found regarding the use of methanol blends in future-type powerplants such as the stratified charge engine. Since this type of engine is expected to be in use if and when blends become available, it is important that its performance and emissions characteristics with blends be ascertained.

As with neat methanol, it is not clear in all cases exactly why the observed changes in performance and emission characteristics occur when methanol blends are substituted for gasoline in unmodified vehicles. While the blend-leaning effect and the increased front-end volatility have been identified as being significant contributors to the observed changes, there are other properties of the blends which should influence performance and emissions, but explicit data could not be found.

One such property is the increased latent heat of vaporization. Ethanol blend data suggest that maldistribution should be a problem with methanol blends. No distribution data for methanol blends were found, however.

Two other properties of methanol blends not understood are flame speed and ignition delay. The greater flame speed of neat methanol at stoichiometric and lean mixtures suggests that blends, especially those with a high methanol content, can be used efficiently at leaner-than-gasoline operation equivalence ratios with a subsequent reduction in emissions. Data, however, were not found to support this. Flame speed and ignition delay also affect optimum ignition timing, effects which have not been determined for methanol blends. If the flame speed of the blends is greater than that of gasoline, there should be a corresponding reduction in best torque spark advance. The limited data available suggest that the flame speeds are lower for the blends or that the ignition delay time is longer. It is fundamental to understand this apparent discrepancy.

A combination of the increased latent heat of vaporization and the combustion characteristics of neat methanol suggests that NO_x emissions should be lower for blends at equal equivalence ratios. Data with blend levels up to about 25% methanol show this not to be the case. The reason for this apparent discrepancy is not understood.

With regard to exhaust emissions, research is needed to determine the changes that occur in the organic species found in the exhaust. The limited data available are not in agreement and no consistent trends can be identified except that there will be an increase in aldehyde and methanol emissions.

In addition to the above-described basic engine research, there are many practical problems associated with the introduction of methanol blends (e.g. cold start, hot start, vapor lock, driveability, engine wear, lubrication, and blend stability), which should be studied. Means of overcoming some of these problems, such as blend stability, must be found if methanol is to become a practical automotive fuel.

The recent increase of interest in the use of methanol as an automotive fuel extender has been brought about by the energy shortage, increased cost of crude oil, and the desire to become more independent of foreign sources of liquid fuels. Methanol can be produced from domestic coal and oil shale. So can synthetic gasoline and distillates which have also been identified as alternative fuels. It is generally accepted that blending with methanol will increase the volatility of today's petroleum-derived gasolines to unacceptable levels for unmodified vehicles. The blending of methanol with coal- or shale oil-derived synthetic gasoline should also increase front-end volatility. This, however, will be beneficial, since synthetic gasolines by themselves would have too low a front-end volatility and it would be necessary to blend in light-end hydrocarbons which may be in short supply. The methanol could be used instead. The higher aromatic content of synthetic gasolines should also improve the blend solubility. It is important that tests similar to those already carried out or recommended above for conventional gasoline-methanol blends also be performed for blends of methanol and synthetic gasolines.

In addition, before a decision is made regarding the use of methanol blends or neat methanol as a fuel of the future, it seems that a comprehensive macroscopic study of the methanol- and methanol-blend-fueled vehicle scenarios should be conducted utilizing a systems dynamic approach such as that developed by Forrester (197, 198, 199). This approach inter-connects concepts from demography, economics, and technology into a model which is essentially a number of multi-loop nonlinear feedback systems. Given the assumption about how the components of the system affect each other, the computer is then used to trace the operation of the system through time. Components of the system would include all aspects of the scenario in which methanol and gasoline are used as fuel ingredients, such as sources of the ingredient, production, transmission, storage, distribution, blending requirement, usage as a fuel, usage as a chemical feedstock, environmental impact and so forth. Such studies are quite complex and require a team of researchers from a wide variety of disciplines. The Stanford Research Institute is reported to be carrying out such a study (197).

IV. C EMISSIONS MEASUREMENTS

From the previous discussions in Section D.it is apparent that emission-measuring-technique research is required in order to completely characterize exhaust emissions from methanol- and methanol-blend-fueled engines.

In order for the FID response to reflect total hydrocarbon emissions, it will be necessary to develop a method which will simultaneously determine the concentration of methanol (and to a lesser extent other oxygenates found in the exhaust), accounting for its reduced sensitivity, and the concentration of the hydrocarbons usually detected by the FID. A promising approach is the development of an "in line" methanol "scrubber" that will permit the intermittent elimination of methanol from the exhaust gases so that a differential analysis may be obtained. This would permit the determination of both total hydrocarbon content exclusive of methanol and methanol content under identical steady-state conditions. A two-detector system would eventually replace the intermittent one after the initial development so as to obtain simultaneous analysis of methanol and total hydrocarbon exclusive of methanol on a continuous real time basis.

With regard to hydrocarbon analysis there also appears to be a need for multidetector differential systems. In such systems "group" scrubbers would be employed to strip-out compound classes (such as aromatics, olefins, etc.). With differential detectors, probably FID, it would be possible to display total hydrocarbon (a), total hydrocarbon minus aromatics (b), and total aromatics (a-b). In this manner continuous real time testing could be carried out while obtaining emission information that is normally not available without resorting to total GC analysis. The differential method would probably require very little modification of normal procedure and could be adapted to most present systems.

An alternate approach would be the use of specific detectors that would be capable of detecting compound classes parallel to the FID total hydrocarbons. Olefins, for example, might be detected by a catalytic chlorinator preceding an electron capture detector. Thus, total olefins could be determined. With this approach a UV technique should also be examined through the second derivative method of a specific wavelength range. Specific compounds could then be determined. For example, formaldehyde could be determined in complex gas samples by determining the second derivative of the signal during a specific wavelength sweep and displayed as a "peak." This method would be of great advantage for specific emission components.

Methods are also needed for continuous real time analysis of aldehydes and other oxygenates found in exhaust emissions. Potential methods are second derivative UV spectroscopy and infra-red (NDIR-DIR), (See Table 7).

In addition, an examination is needed of the use of instrumentation such as quadrupole mass spectroscopy, Fourier transform, IR and second-derivative UV, combined with continuous real time data acquisition, storage and display as a means of obtaining continuous real time analysis of complex exhaust emissions. Although these methods involve considerable capital investment, they may prove to be most adaptable. For example, quadrupole mass spectroscopy, with low ionization electron excitation, could scan complete exhaust mixtures in milliseconds. With in-line computer capabilities and component sensitivities, it would be possible to solve complex mixture problems giving a continuous real time, complete analysis of complex exhaust mixtures. Such a system would require extensive research, development, time and effort. In the long run, though, such methods may turn out to be completely adaptable to further studies with other potential substitute fuels and engine design.

IV. D MATERIALS COMPATIBILITY

The results of this survey on the use of methanol or methanol-gasoline blends leave many questions unanswered regarding the compatibility of these fuels with automotive materials. Moreover the inconsistencies reported add to the confusion and cause doubt as to whether these fuels can be used either by the general public or in special fleets.

To evaluate the effect of the methanol fuel on the materials in the fuel system many questions must be answered. Of primary importance is the question of the chemical reactions which take place over an extended period of time between the fuel and such materials. As there is some uncertainty as to the amount of water which will be absorbed by the fuel, the chemical reactions must be evaluated over the range of water concentration which can be expected to be present in the fuel under practical use.

From a practical standpoint, it must be assumed that any fuel containing any amount of methanol must be exposed to moisture and will thus absorb water into the fuel. The amount of moisture absorbed will depend on many factors and cannot be accurately predicted. In fact, the amount will probably vary depending on length of storage, location, humidity, etc.

In addition to chemical reactions, electrochemical relationships are very important. In a fuel system there are several different metals, each with its own electrochemical potential, connected by an electrolyte - the fuel. A study of this relationship is necessary in order to evaluate the practical use of a new fuel. Areas of question for compatibility of materials are fuel tank, fuel lines, fuel pump, and carburetor.

Since chemical reactions are greatly affected by temperature, the temperature range which can be expected in practical use must be evaluated. The time of the tests must be such that a reliable prediction of the reaction over the life of the automobile can be obtained. In addition, as an automobile is usually mobile, the effect of agitation as it affects the chemical reaction must be evaluated.

Other questions which are unanswered at present concern the magnitude of the chemical attack of the fuel on the materials used in the fuel system. The reported attack is only a small amount but whether this amount will be significant in the expected life of an automobile has not been determined.

Another area of doubt is the effect of the fuel on engine wear. Wear is primarily a function of engine use - that is, time in operation and energy (horsepower) output. However, it is a complicated process and depends on many factors. With the addition of methanol as a fuel, products of combustion are changed and the wash-down of the cylinder walls is changed. Also changed are the operating temperatures and the reaction of the fuel with lubricant. All of these factors can significantly affect wear inside the engine.

Information is necessary in order to evaluate the effect of methanol-gasoline blends as compared to gasoline fuel on wear. As the piston rings are the most susceptible part for engine wear, an evaluation of ring wear as a function of fuel composition is necessary. An additional area of wear is the valve guides. It may be necessary to evaluate both ring wear and valve guide wear to fully understand the role of the fuel on engine wear.

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SYMBOLS AND ABBREVIATIONS

AF	Air Fuel Ratio
B	Blend
bhp, BHP	Brake horsepower
bmep	Brake mean effective pressure
BOV	Blending Octane Valve $\equiv \frac{(ON)_B-[(1-f)\ (ON)_{Base\ G}]}{f}$ where f is the fraction of the blending component, values are presented as either research method BOV denoted with an R or motor method BOV denoted with an M.
bsfc, BSFC	Brake specific fuel consumption $\frac{lbm}{hp-HR}$
BTDC	Before Top Dead Center
CFR	Cooperative Fuel Research Council, usually used to refer to single cylinder octane rating engine.
Chemi	Chemiluminescent NO_x analyzer.
CLR	Cooperative Lubricant Research (engine)
c_p	Specific heat at constant pressure
CR	Compression Ratio
c_v	Specific heat at constant volume
DIR	Dispersive Infrared Analyzer
E	Ethanol
EGR	Exhaust Gas Recirculation
f	mole fraction
FID	Flame Ionization Detector
G	Gasoline
GC	Gas Chromatograph
h	Enthalpy
HC	Hycrocarbon
h_{lv}	Latent heat (enthalpy) of vaporization.
HV	Heating Value
I	Isooctane
ihp, IHP	Indicated Horsepower
isfc, ISFC	Indicated specific fuel consumption $\frac{lbm}{hp-HR}$
$\dot{m}$	Mass flow rate
M	Methanol
MBOV	See BOV
mbt	Minimum spark advance for best torque

mep	Mean effective pressure
mf	Mass fraction
mi	Miles
M_i	Molecular weight of species i
mm hg	Millimeters of mercury
MON	Motor Octane Number
mpg	Miles per gallon
NDIR	Non-Dispersive Infrared
p	Proof e.g. 190pE denotes 190 proof ethanol
P	Pressure
r	Compression ratio
RBOV	See BOV
RDH	Removable Domed Head (engine)
RON	Research Octane Number
RPM	Revolutions Per Minute
RVP	Reid Vapor Pressure
SA	Spark Advance, deg. BTDC
SAE	Society of Automotive Engineers
sfc, SFC	Specific Fuel Consumption
SG	Specific Gravity
t	Time
T	Temperature
tel	Tetraethyllead
Vf	Volume fraction
WOT	Wide Open Throttle
%M or %E	Refers to the volume percent of Methanol (or Ethanol) in an Alcohol-Gasoline blend

GREEK SYMBOLS

γ	Specific gravity
η_b	Brake thermal efficiency
η_i	Indicated thermal efficiency
η_t	Thermal efficiency
η_v	Volumetric efficiency
ϕ	Fuel-air equivalence ratio

SUBSCRIPTS

a	Air
air	Intake air
B	Blend
exh	Exhaust gas
f	Fuel
G	Gasoline
I	Isooctane
M	Methanol
man	Manifold
mix	Fuel-Air Mixture
w_j	Water Jacket

Table 1 Power Output Alcohol vs. Gasoline @ Equal CR.

ETHANOL NEAT

Ref.	Author	Fuel	No. Cylinders	% increase
33	Lichty & Ziurs	190 p	1	1.5 3.2
48	Ricardo & Glyde	196 p 190 p	1	4.6 8.2
52	Brooks	190 p 200 p	1	5.2 4.5
53	Duck & Bruce	190 p 200 p	various, multi.	0.6 to 3.1 1.1 to 5.6
103	Starkman		1	4%

METHANOL NEAT

Ref.	Author	No. Cylinders	% increase
48	Ricardo, Glyde	1	10.3
103	Starkman,et al.	1	9
125	Pefley et al.	1	-5
129	Ebersole & Manning	1	0
158	Bernhardt & Lee	4	10

Table 2. SFC, MPG, Efficiency Ratios (Alcohol/Gasoline) @ Equal CR

ETHANOL NEAT

Ref.	Author	Proof	No. Cylinders	ϕ*	Sfc	mpg	η
33	Lichty, Ziurys	190	1 1 6	1 MP MP	1.7 1.6 1.58 to 1.63		
48	Ricardo,Glyde	196 190	1 1	ME ME			1.019 1.022
52	Brooks	190 200	1 1	MP MP	1.65 1.54		1.04 1.03
53	Duck, Bruce	190 200	multi 4	ME ME			1.009 to 1.033 1 to 1.028
103	Starkman,etal.	200	1	ME			0.861
122	Keller,et al.	200	multi-road tests multi-lab tests			0.68 0.58	1.024 0.873

METHANOL NEAT

48	Ricardo, Glyde		1				3.2
103	Starkman,et al.		1	BE			1
128	Adelman,et al.		6	70mph		0.53	1.058
125	Pefley,et al.		1				1
129	Ebersole, & Manning		1		2.15		1.04 to 1.05
171	Jackson, & Tillman	see Appendix A					
158	Bernhardt,Lee				1.92		1.14

* MP = Maximum Power ϕ
ME = Maximum Efficiency ϕ

Table 3. Equivalence Ratios for Maximum Power (MP) and Maximum Efficiency (ME)

ETHANOL NEAT

Ref.	Author	Fuel	No. Cylinders	Φ @ MP	Φ @ ME
33	Lichty, Ziurys	190pE	1	1.21	
		Gasoline		1.26	
53	Duck, Bruce	200pE	multi		0.75 to 0.86
		Gasoline			0.84 to 0.91
103	Starkman, et al.	200pE	1		0.9
		Isooctane	1		0.9

METHANOL NEAT

103	Starkman, et al.	Methanol Isooctane	1 1		0.82 0.90
129	Ebersole and Manning	Methanol Methanol	1 1		0.88 @ 1800 RPM 0.80 @ 1000 RPM
155	Adt	Methanol	4		0.78

Table 4 Selected Methanol Data from Ebersole and Manning (129) (N = 1000 RPM, CR = 7.5)

Fuel	I*	M**	M	I	M	I	M
Run No.	76	134	108	63	110	71	28
ϕ	1.004	1.000	0.77	0.996	0.964	1.004	0.989
imep,psi	64.5	66.3	64.9	78.2	76.7	115.7	113.0
Sfc,16/hp-hr	0.395	0.828	0.79	0.391	0.812	0.393	0.823
SA, deg BTC	35	25	35	32.5	27.5	30	25
CO gm/ihp-hr	8.4	5.5	1.9	12	1.6	8.4	4.0
NO_x "	9.02	7.06	5.26	8.69	8.83	10.25	10.48
HC "	2.66	0.34	0.37	2.12	0.28	1.52	0.25
HCHO "	0.09	0.188	0.235	0.097	0.204	0.087	0.163

* I - Isooctane

** Methanol Neat

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Table 5 Thermal Efficiency, bsfc and mpg Ratios (Blend/Gasoline)

ETHANOL BLENDS

Ref	Author	Blend % E	No. Cyl.	Carburetion	SA	Sfc Ratio	Mixture	η Ratio		CR
32	Egloff & Morrell	10 10	Various Multicyl.			1.04 1.05		1.03	Road & Block Tests	Equal HUCR
29	Bridgeman	10 and sometimes 20 10 20	Multicyl. " "	Average Optimum "	Average Optimum "	1.0 1.03 to 1.04 1.06 to 1.08			Similar power, acceleration " " " " " "	Equal Equal Equal
31	Christensen	Up to 25		Stock	Stock	possible decrease			Road Tests	Equal
42	Lichty and Phelps	10 E anhydrous 20 10 20	1 1 6 6	min bsfc min bsfc max power & min bsfc	Optimum " " "	1.057 1.103 1.0 1.09		1.03 1.09 ≈ 1.0* ≈ 1.0*	Engine Dynamometer " " "	Equal " " "
101	Lawrason, Finigan	25 200_pE " " 25 200_pE 23 190_pE	8 8 8 8	Stock " " "	Stock " "	1 1.12	≈1.0 ≈0.9	(1.16)** (1.04)** (≈1.07 (≈0.99)	WOT engine dyno. ¼,½,3/4 of WOT Road load up to 70mph " " up to 70mph	10.25 10.25 10.25 10.25
122	Keller et al.	10 25 10 25 10 20 30		Stock Stock Max Power Max Power	Optimum " " "	1.013 1.048 1.052 1.001	0.984 0.962 0.936	>1 >1 >1 >1 >1 >1 >1	Avg. of road & lab.tests " " " " " " " " " " " "	
				METHANOL BLENDS						
134	Texaco	20	1	Equal ϕ	21°BTC	1.15	0.88	(0.97)** (≈1.12)**		
	1932 British data	10	1	Stock		≈1.0	0.94 to 0.99	102 to 1.07	5 cars, road tests	Equal
170	Ingamells, Lindquist	10	Multi	Stock	Stock		1.0 to 1.19		5 cars, road tests	Equal
176	Reed et al.	0 to 30	Multi	Stock	Stock		1.08	(1.16)**	ECE Test Procedure	Equal
169	Heitland et al.	15	Multi	Stock	Stock			≈ 1		
184	Colucci	10	16 Multi	Equal ϕ	Stock					

*Efficiency with blend increased if blends allowed use of more nearly optimum spark advance.

**Efficiency ratios in parenthesis estimated from given sfc or mpg data and Figures 8 and 9.

Table 6 Federal Emission Standards and Emissions from Methanol and Methanol Blends (gm/mi)

			HC	CO	NO_x	Aldehydes+
1975 Standards			1.5	15	3.1	
1976 Standards			0.41	3.4	2.0	
1977 Standards			0.41	3.4	0.4	
METHANOL NEAT						
Adelman et al.(128)	9 x 7 Cold Start CVS		0.32	3.87	0.39	
METHANOL BLENDS						
Texaco (134)	FTP Hot Cycle	Gasoline	2.04	39.65	5.59	
		20% M*	2.27	38.98		
		20% M**	1.58	18.70	4.47	
Pefley (183)	CVS Hot Test	Gasoline	2.51	58.8	3.32	
		10% M	1.97	42.5	2.53	
	CVS Cold Test	Gasoline	2.94	66.3	4.74	
		10% M	2.81	75.5	3.23	
	'67 Auto,FTP	Gasoline(rich)	5.2	83	6.4	0.13
		15% M	3.8	41	8.1	0.20
Esso (190)	'73 Auto, FTP	Gasoline(lean)	1.1	21	2.6	0.075
		15% M	1.1	8	1.7	10
	'75 Auto, Catalyst, FTP	Gasoline($\phi \approx 1$)	0.1	0.3	2.6	0.002
		15% M	0.1	0.4	2.3	0.004

*Good performance

**Poor performance

+ Calculated as Formaldehyde

le 7. Summarizes Emission Measuring Techniques

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CONTINUOUS REAL TIME METHODS

ission Specie	Method	Comments
CO	Infra-red (NDIR-DIR)	Methods standardized and acceptable - commercial units available.
CO$_2$	Infra-red (NDIR-DIR)	Methods standardized and acceptable - commercial units available.
NO	Chemiluminescence	Methods standardized and acceptable - commercial units available.
	Infra-red (DNO)	Method acceptable. No need for pre-detector dessicant
NO$_2$	Chemiluminescence	Method dual with NO analysis.
Total Hydro-carbons	FID	Carbon equivalent detector. Non specific; the total signal depends on the average carbon number of the emission sample. Reduced sensitivity for compounds containing N, O, and other atoms.
	Infra-red (NDIR)	As with FID detection is non-specific; yields results comparable to those of the FID. Suffers from reduced sensitivity (similar to FID).
Methanol	Infra-red (NDIR-DIR)	Potential. Detectors not commercially available; exploratory at present.
Aldehydes and Oxygenates	Second Derivative - UV Spectroscopy	Potential method. Specific for Formaldehyde, Acetaldehyde and many other compounds. Exploratory at present. Must be tuned for each compound individually. Commercial instrument available.
	Infra-red (NDIR-DIR)	Potential method. Exploratory at present.

DISCONTINUOUS DELAYED TIME METHODS

Hydrocarbons	Chromatography (GLC-GC)	Only method for complete analysis of individual hydrocarbons; gives total hydrocarbons and components. Time-consuming.
Methanol	GLC-GC with Ionization Detectors	Present method for analysis of methanol. Needed for correcting data from the FID total HC analyzer.
Aldehydes and Oxygenates	GLC-GC with Ionization Detectors	Present method for analysis of aldehydes and oxygenates. Flame ionization detector shows greatly reduced sensitivity to most oxygenates.

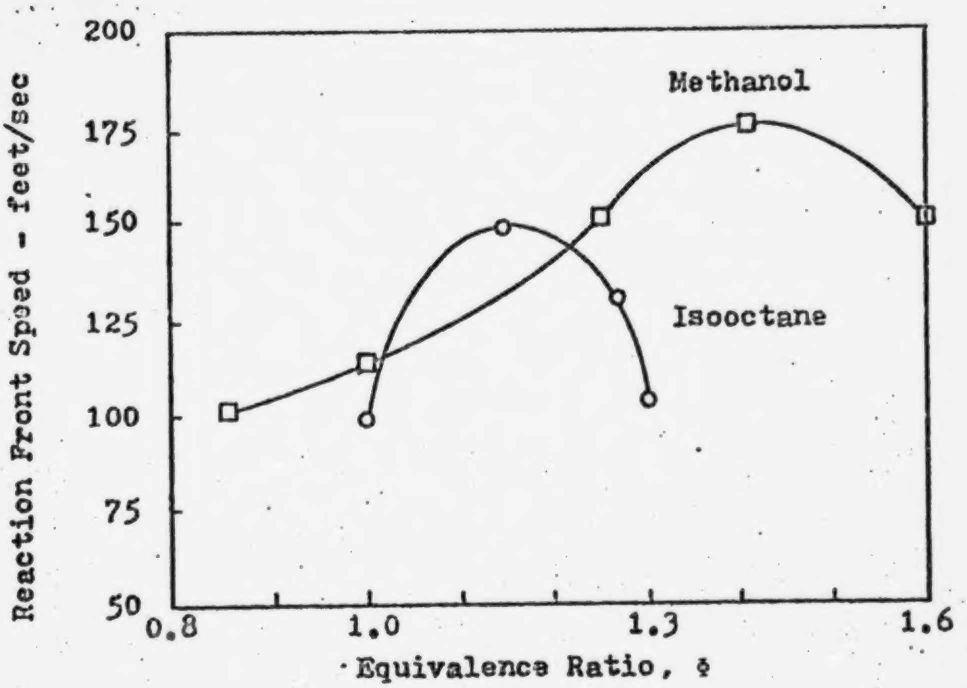


Figure 1 - Reaction Front Speeds for Selected Fuels (85)

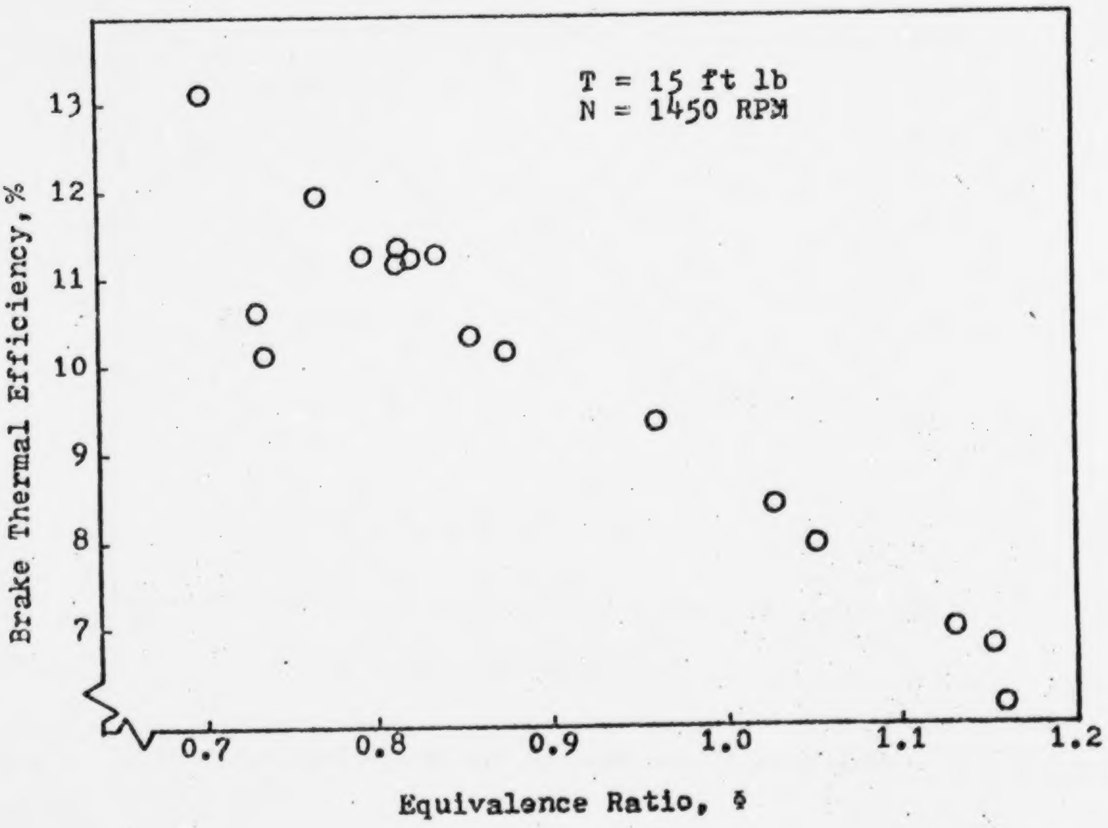


Figure 2 - Brake Thermal Efficiency Versus Equivalence Ratio at 15 ft lb and 1450 RPM for Methanol (155)

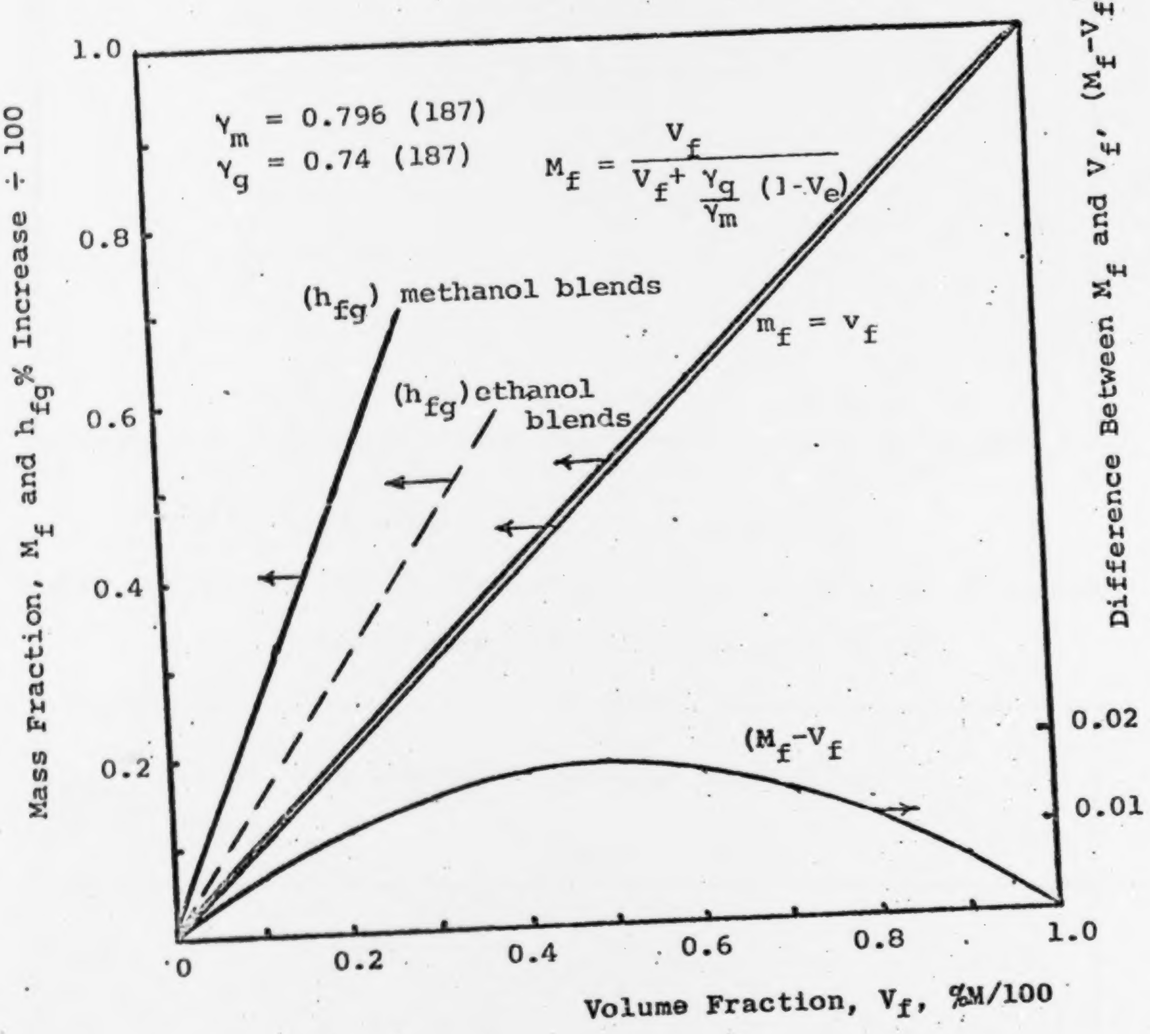


Figure 3 Mass Fraction and Difference Between Mass Fraction and Volume Fraction vs. Volume Fraction (%M/100) for Methanol-Gasoline Blends.

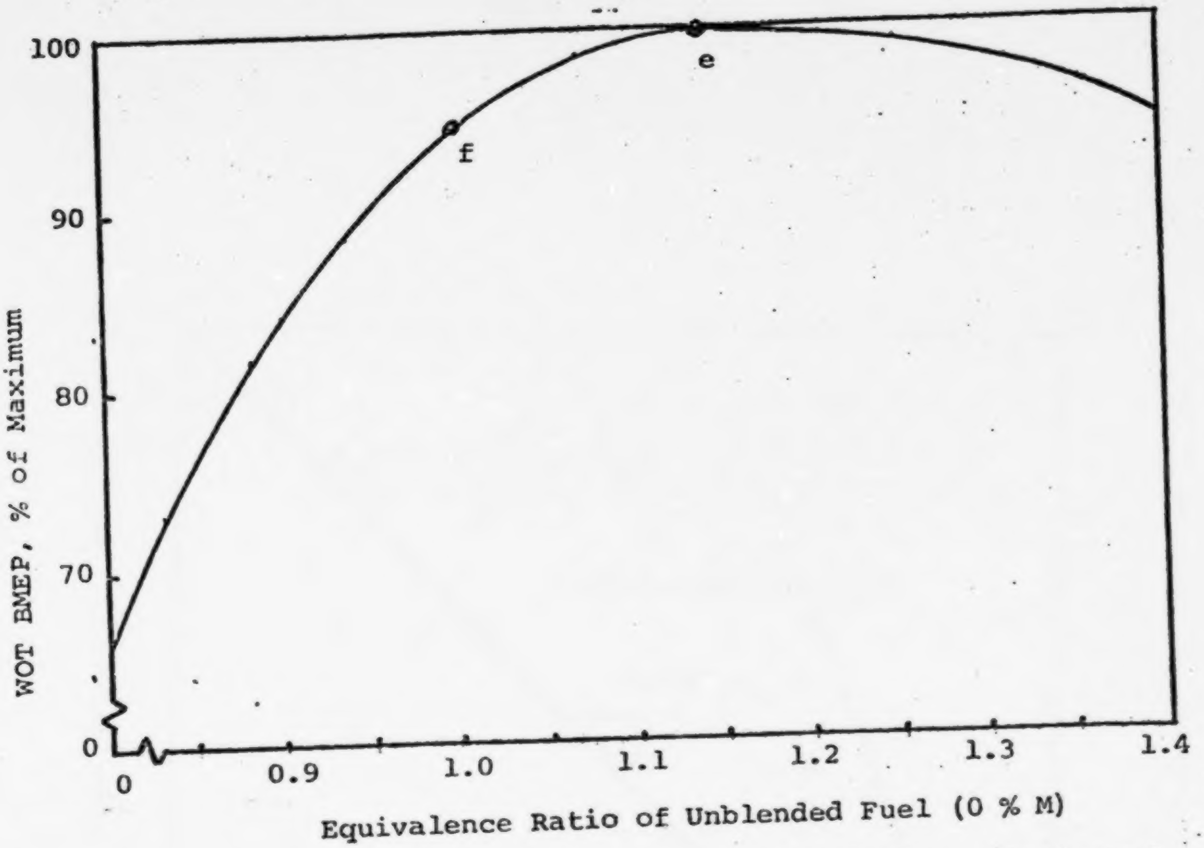


Figure 4 Typical Relationship Between Equivalence Ratio and Brake Mean Effective Pressure (114).

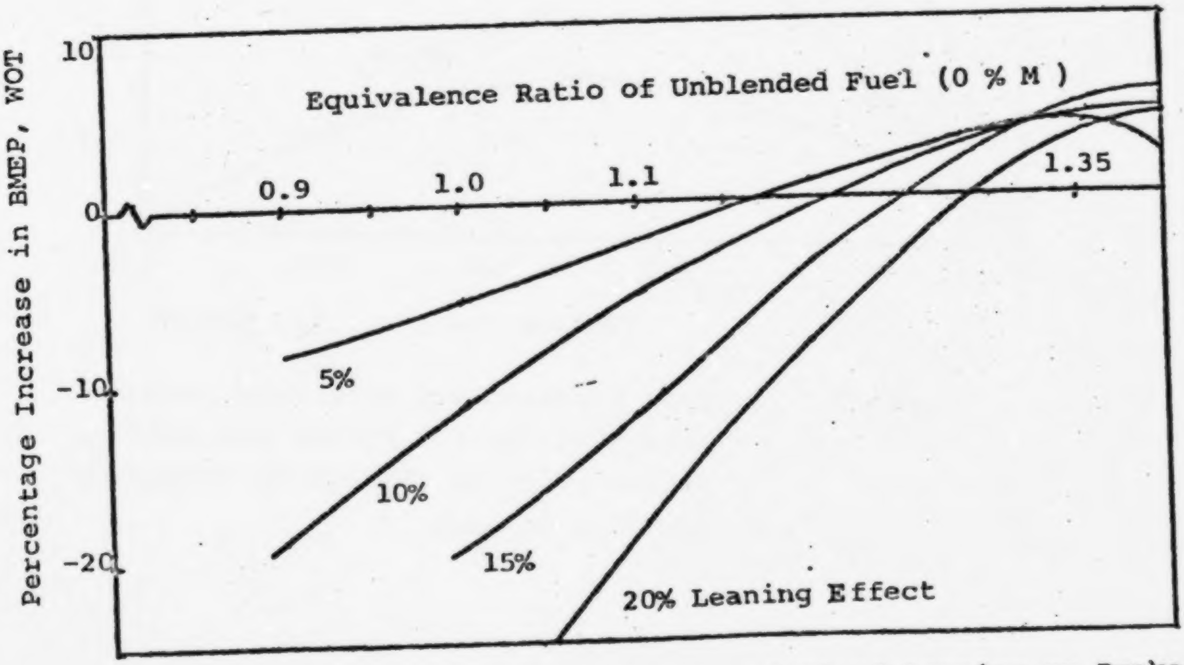


Figure 5 Illustrates the Influence of Blend Leaning on Brake Mean Effective Pressure for 5, 10, 15 and 20% Bler

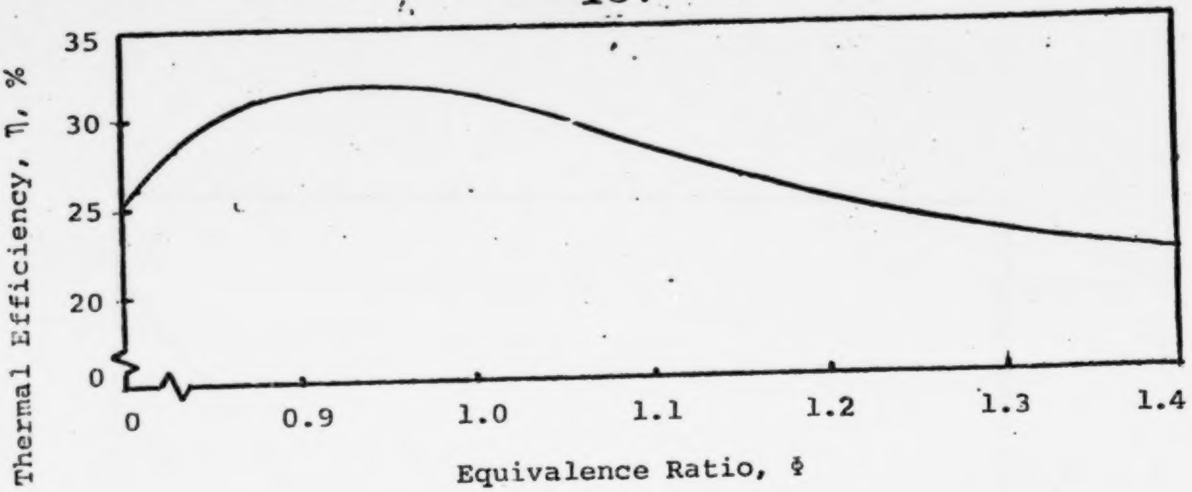


Figure 6 Typical Relationship between Thermal Efficiency and Equivalence Ratio (114).

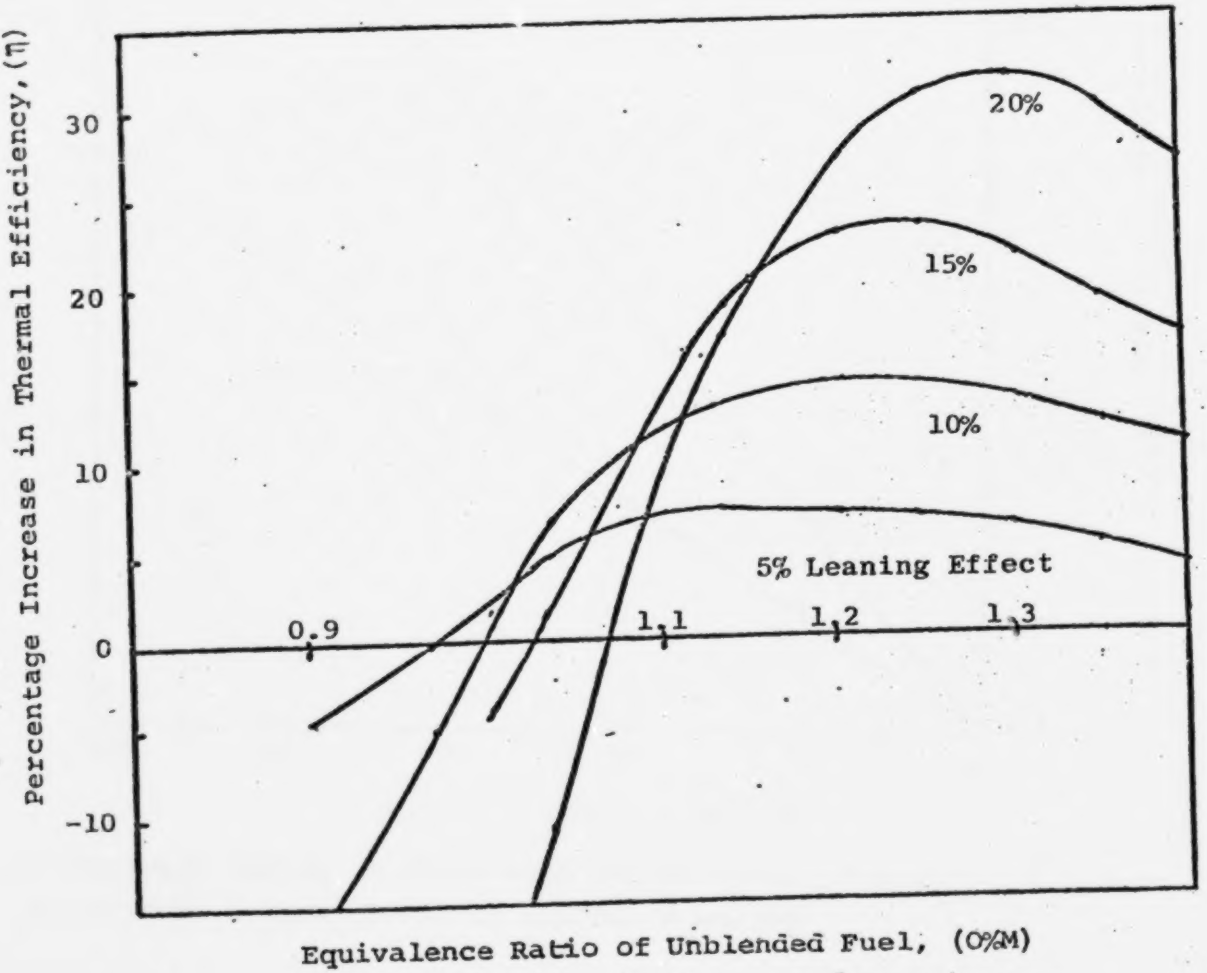


Figure 7 Illustrates the Affect of Blend Leaning on Thermal Efficiency for 5, 10, 15 and 20% Blend

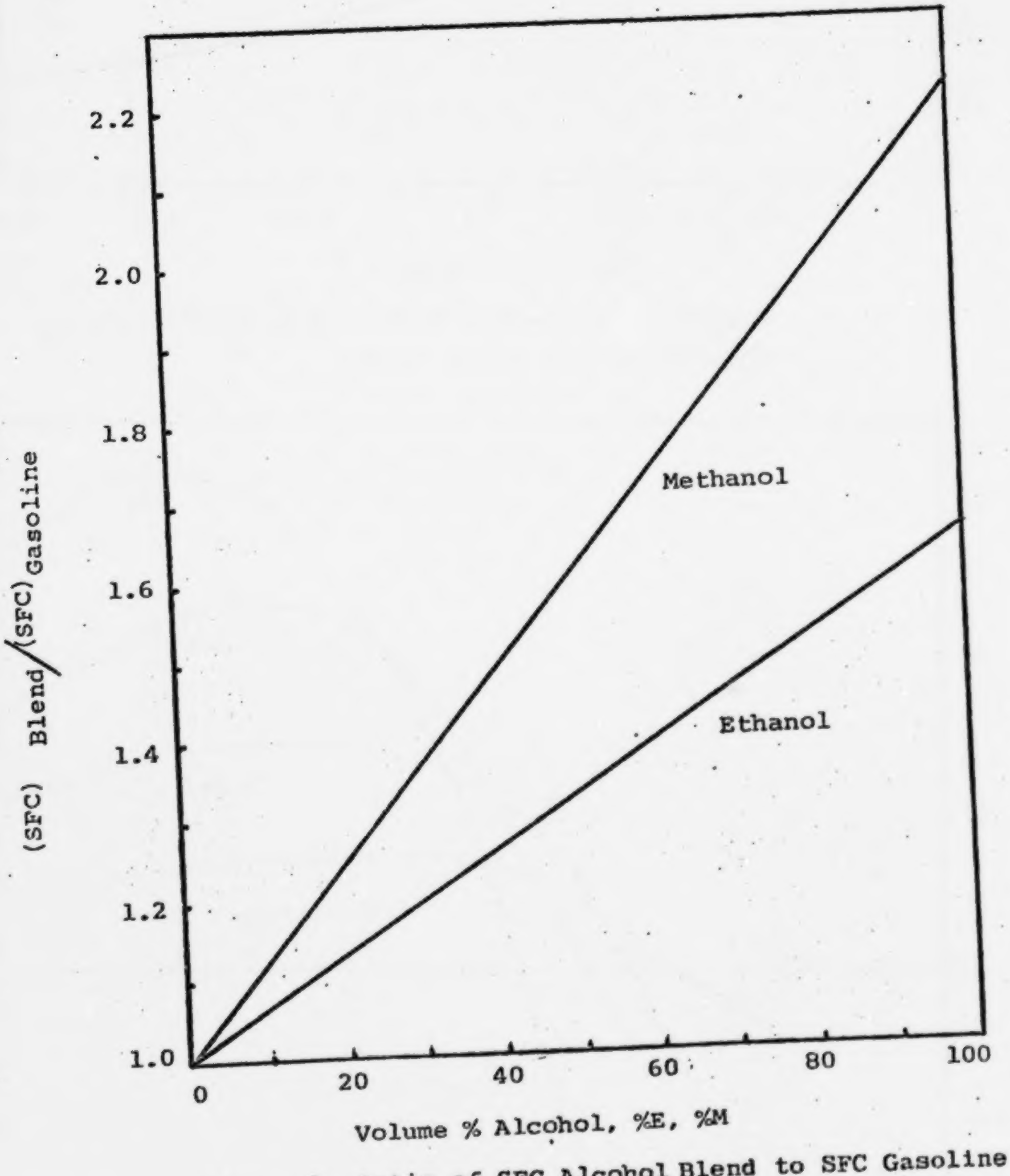


Figure 8 Ratio of SFC Alcohol Blend to SFC Gasoline vs. Volume % Alcohol at Equal Thermal Efficiency.

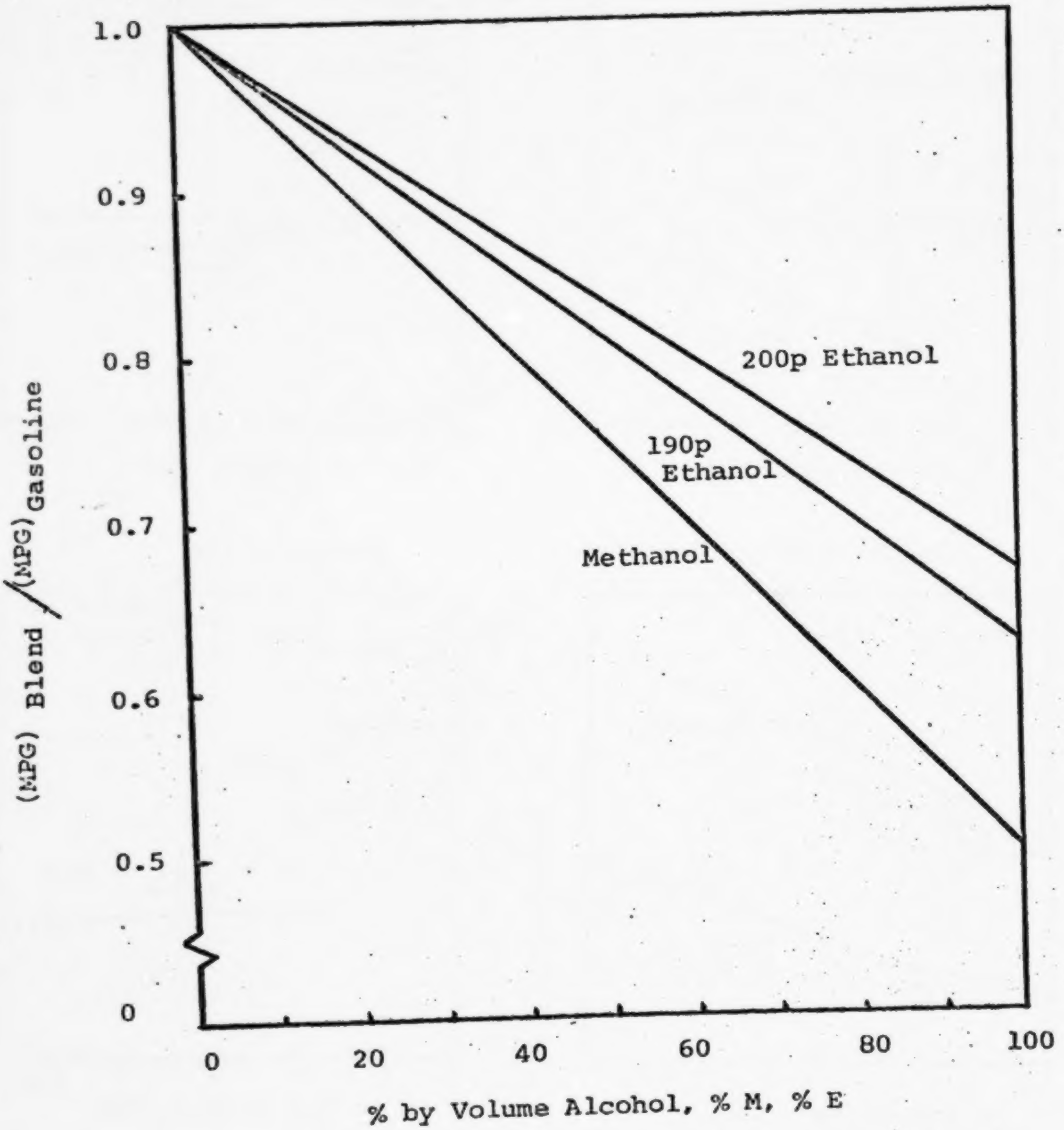


Fig. 9 Ratio of MPG Alcohol Blend to MPG Gasoline vs. Volume % Alcohol at Equal Brake Thermal Efficiency.

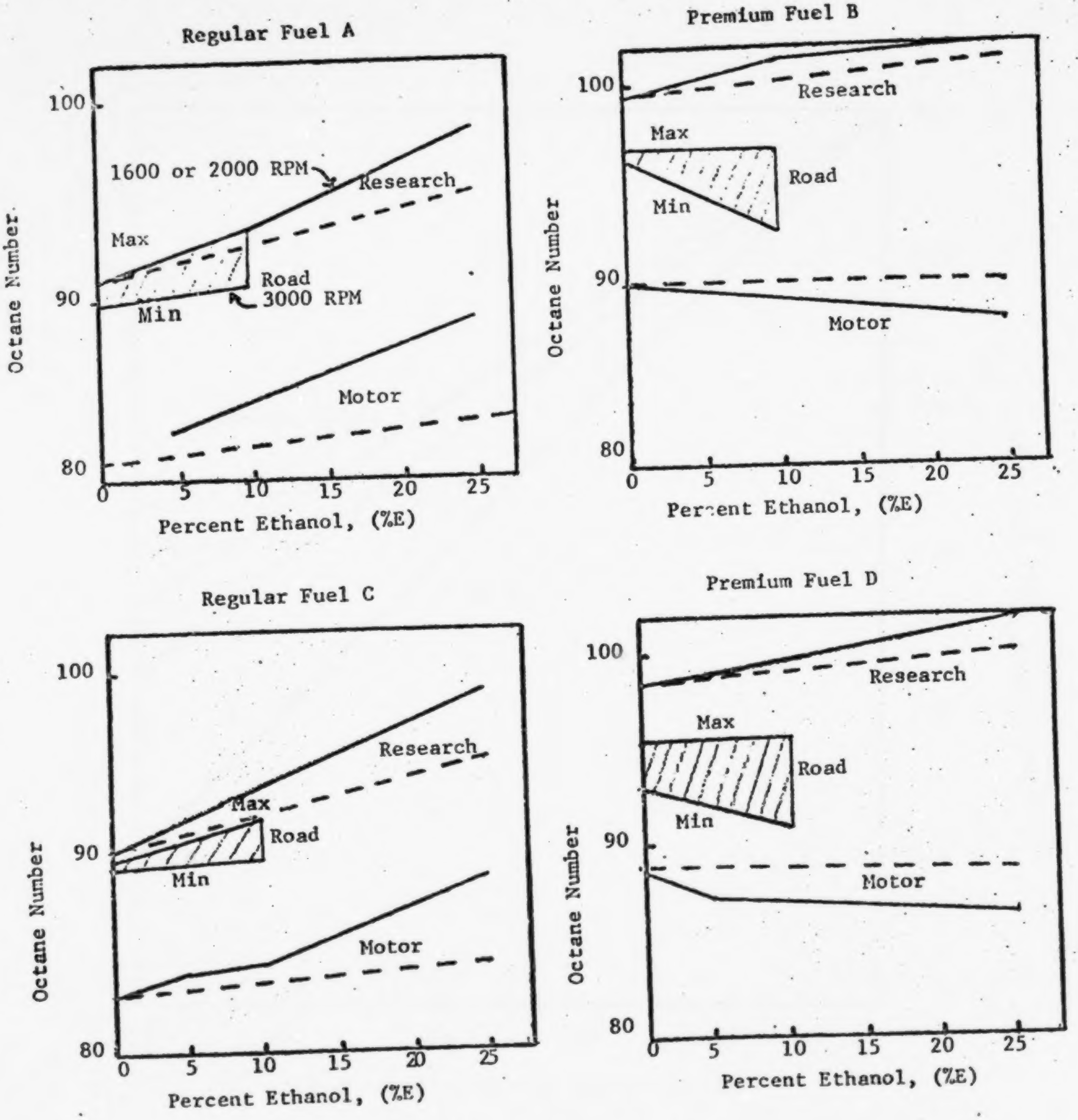


Figure 10 Summary of Fuel Antiknock Ratings. Dashed Lines --- are for the Linear Variation of Octane Number with the Percent Ethanol, (%E); Ethanol : MON = 89, RON = 106.

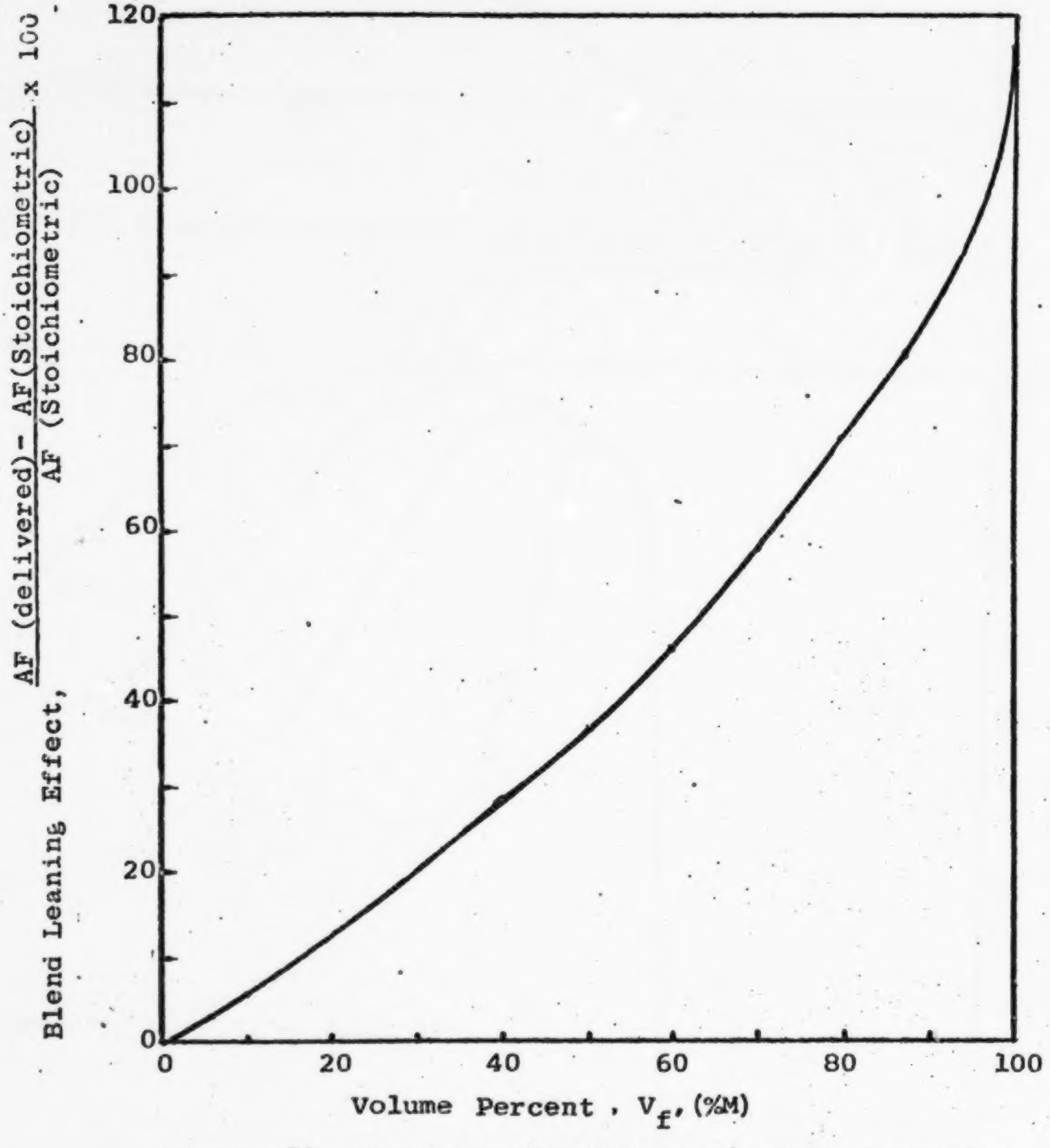


Figure 11 Blend Leaning Effect vs. Volume Percent of Methanol, (%M), in Isooctane.

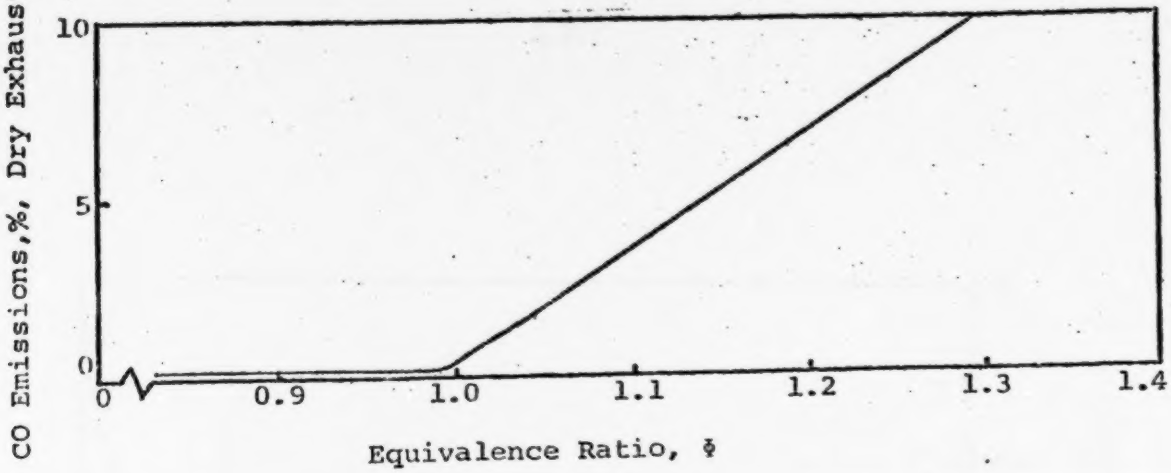


Figure 12 Typical Relationship Between Equivalence Ratio and CO Emissions (119)

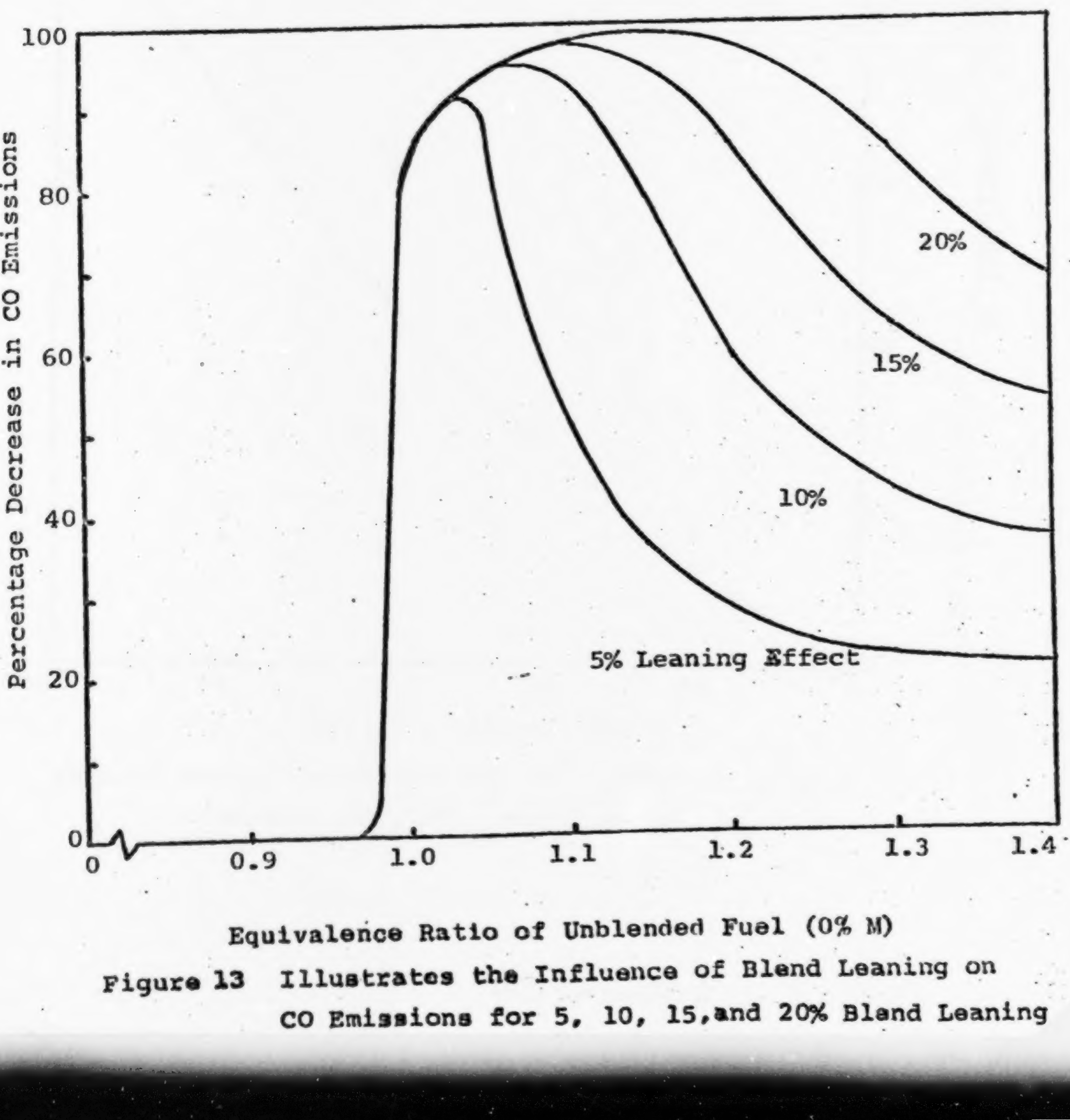


Figure 13 Illustrates the Influence of Blend Leaning on CO Emissions for 5, 10, 15, and 20% Blend Leaning

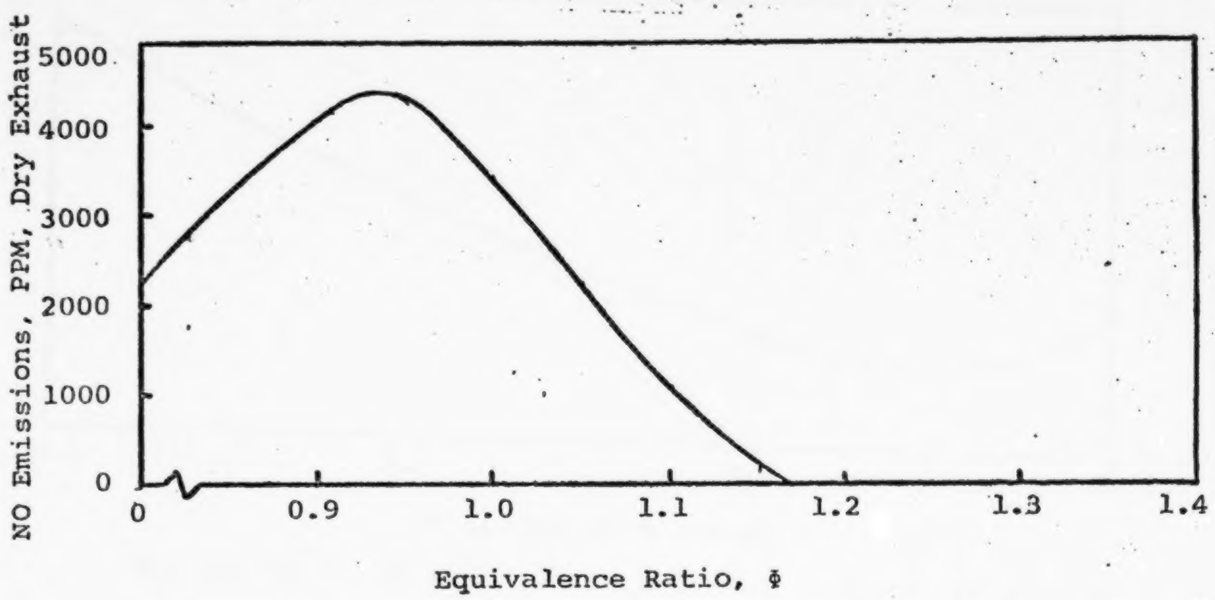


Figure 14 Typical Relationship Between NO Emissions and Equivalence Ratio (119)

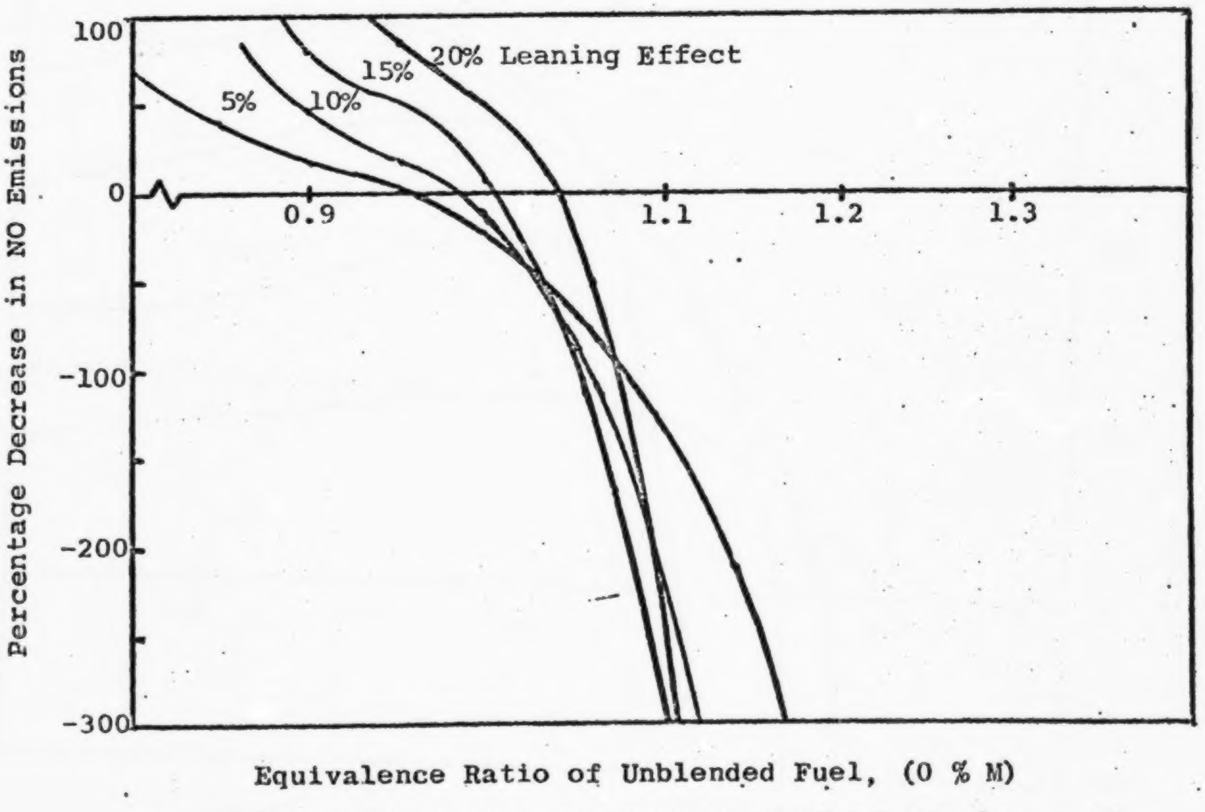


Figure 15 Illustrates the Affect of Blend Leaning on NO Emissions for 5, 10, 15 and 20% Blend Leaning Effects.

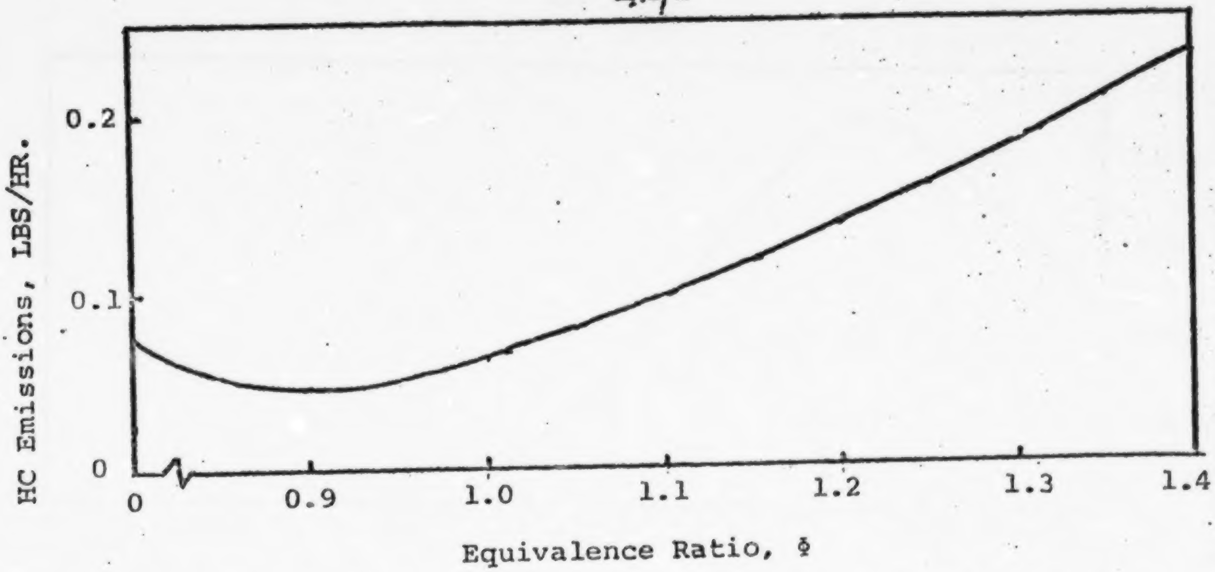


Figure 16 Typical Relationship Between HC Emissions and Equivalence Ratio (131)

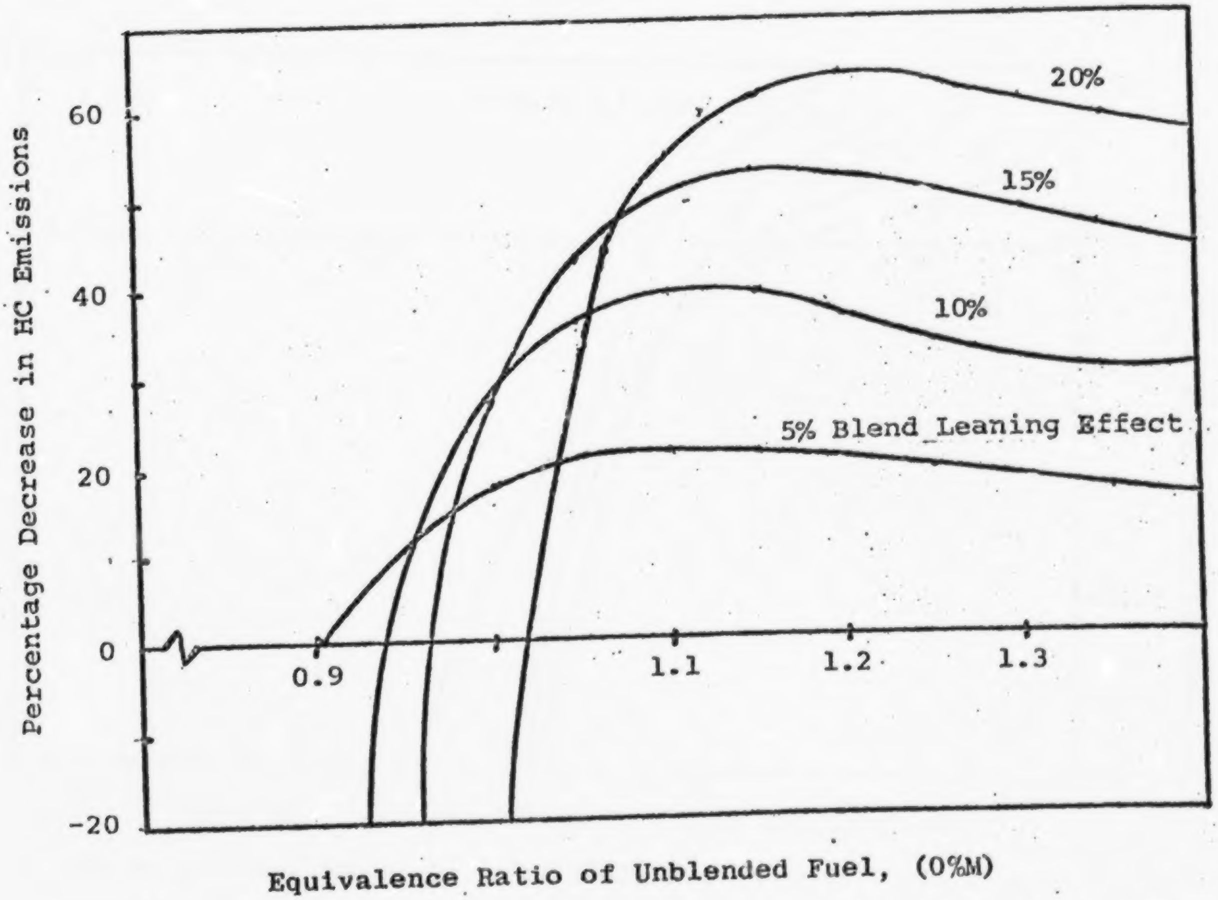


Figure 17 Illustrates the Influence of Blend Leaning on HC Emissions for 5, 10, 15, and 20% Blend Leaning Effects

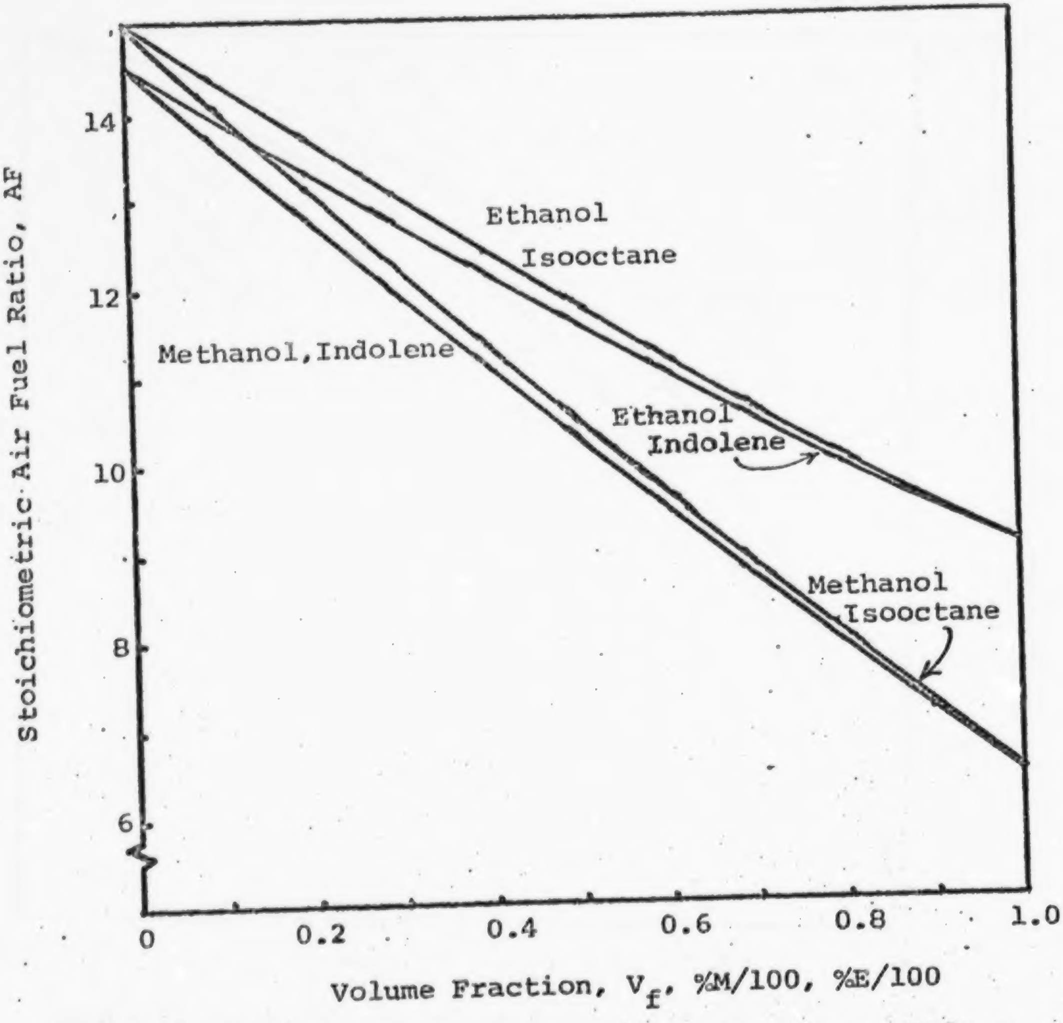


Figure 18 Stoichiometric Air Fuel Ratio vs. Volume Fraction for Methanol in Isooctane and Indolene, and for Ethanol in Isooctane and Indolene.

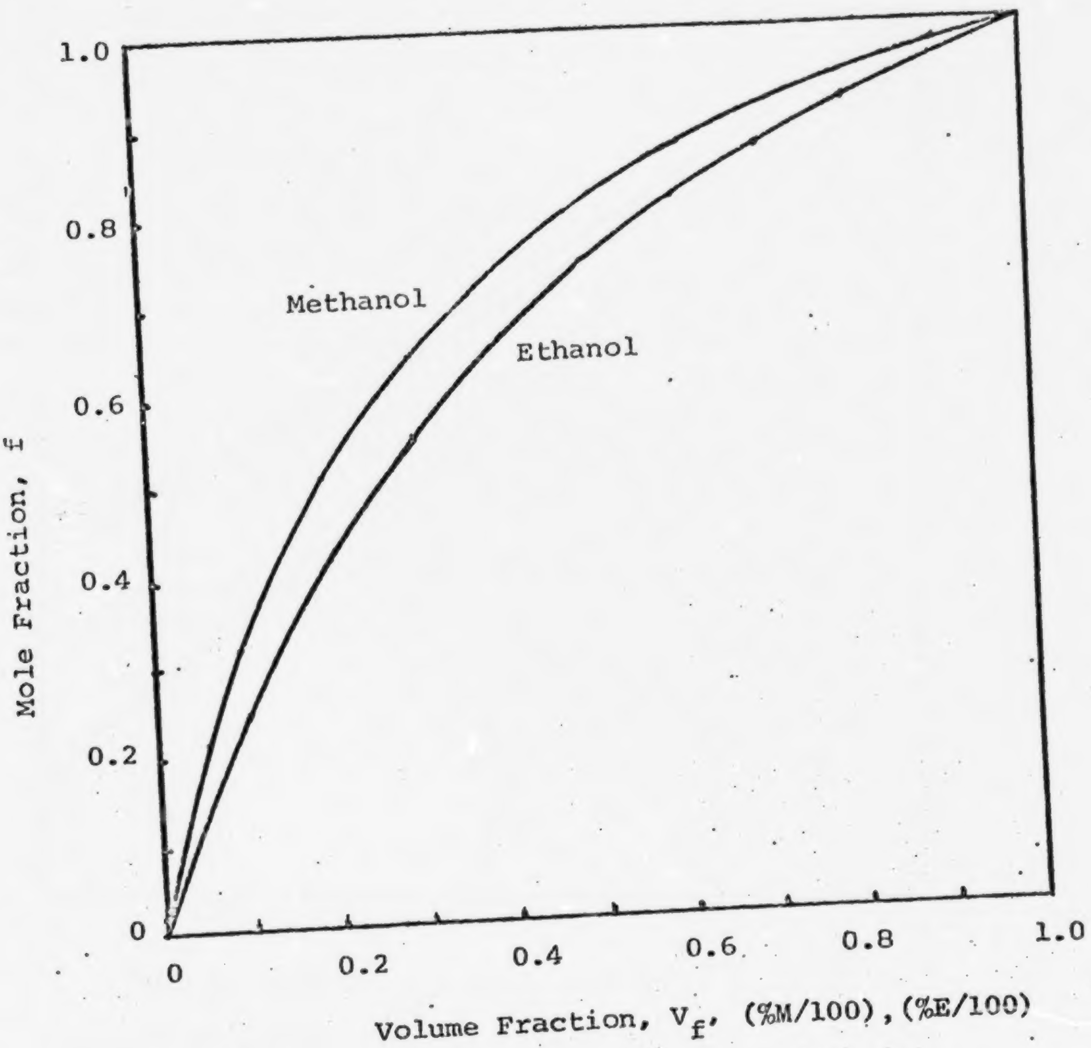


Figure 19 Mole Fraction vs. Volume Fraction for Ethanol and Methanol Mixed with Isooctane.

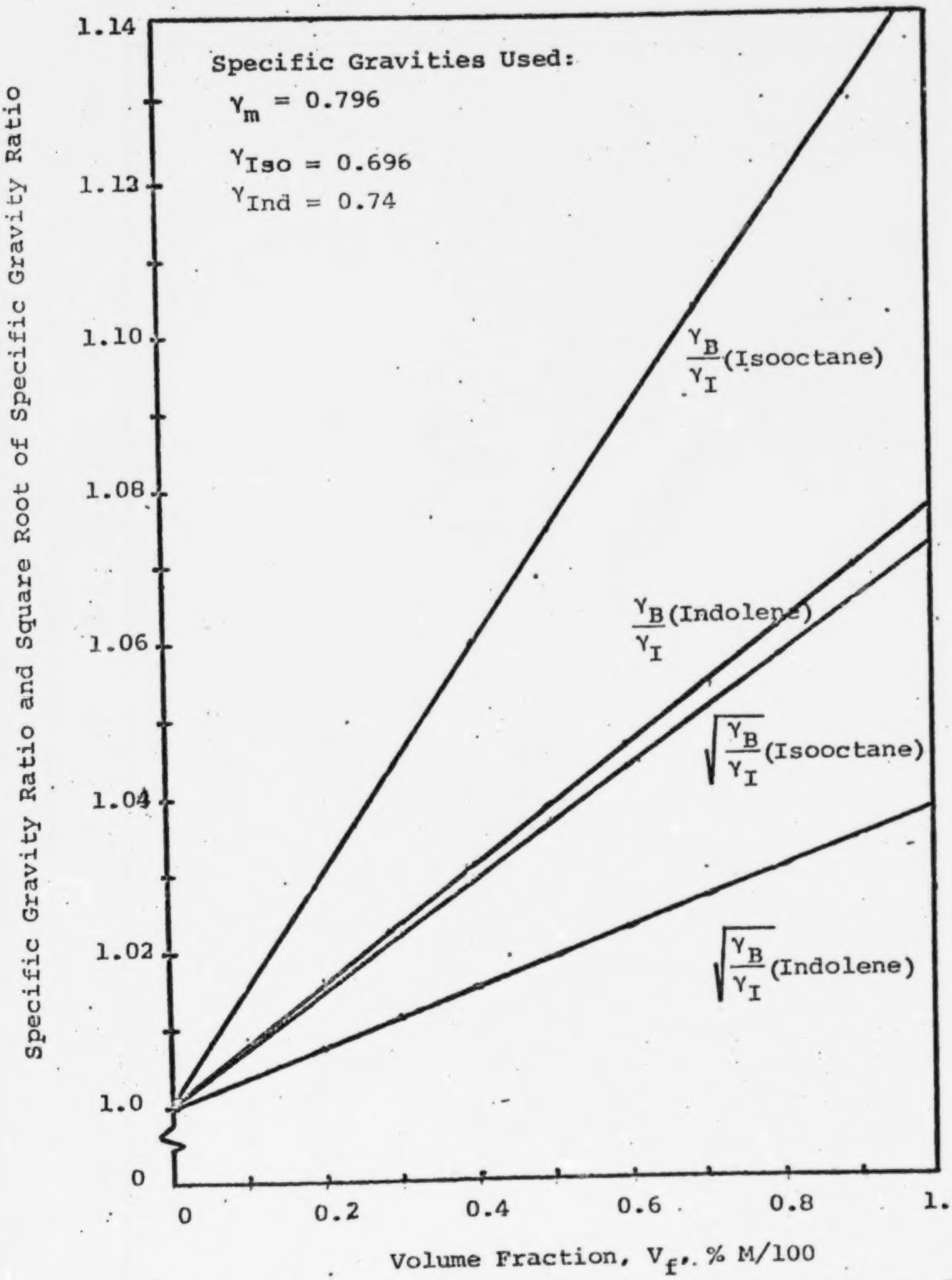


Figure 20 Specific Gravity Ratio and Square Root of Specific Gravity Ratio vs. Volume Fraction of Methanol (% M/100).

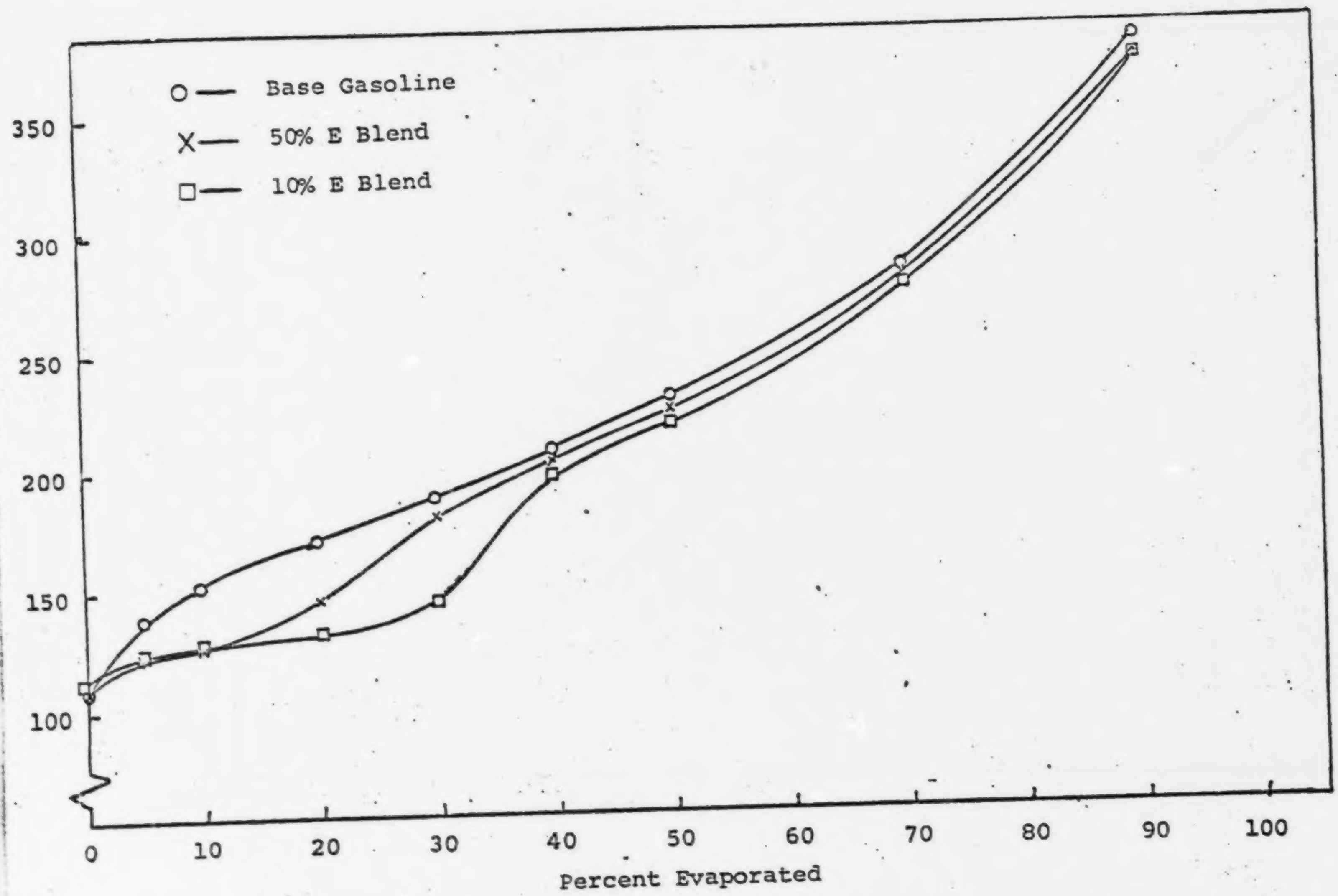


Figure 21 a Distillation Curves for Gasoline and Ethanol Gasoline Blends (144)

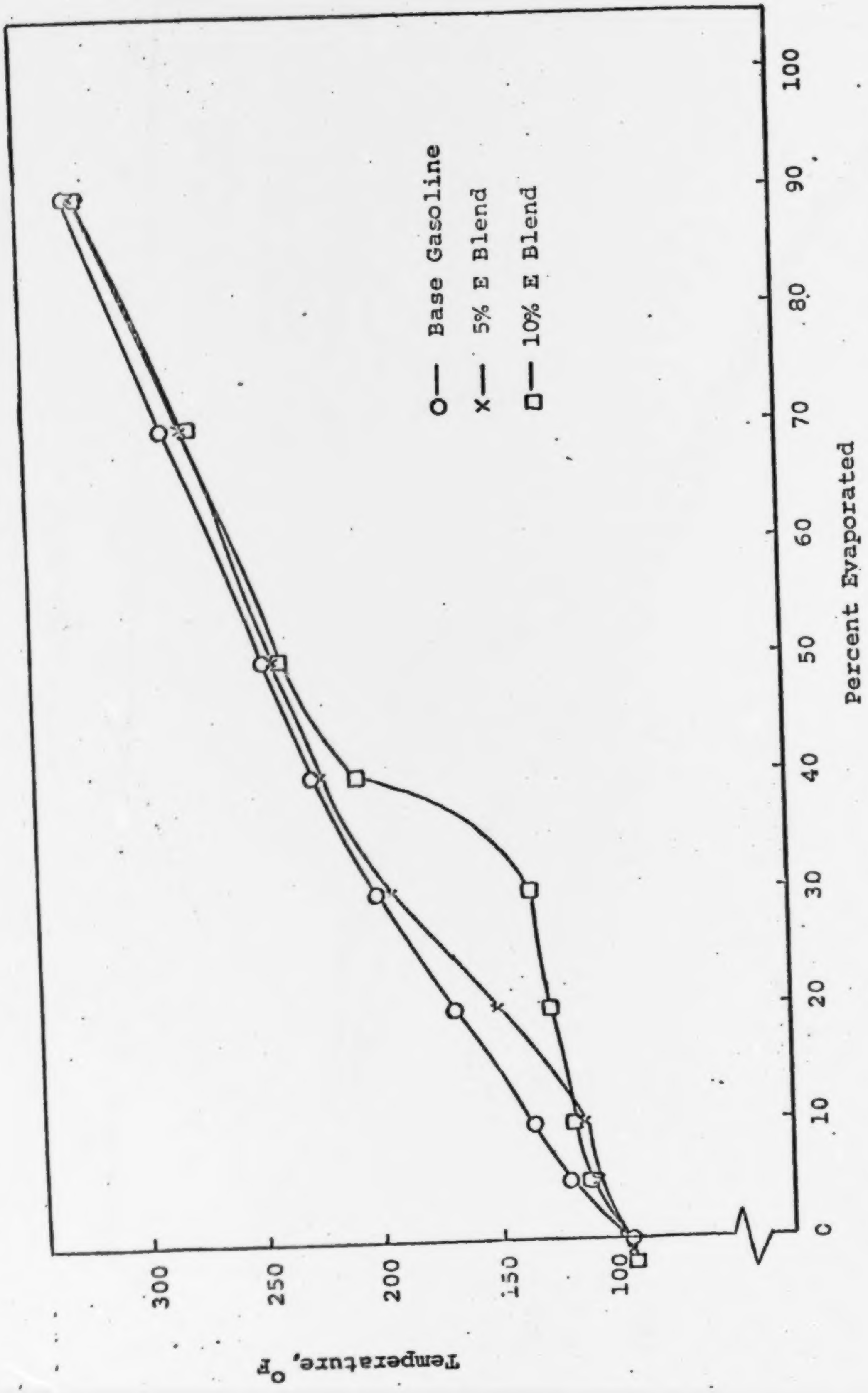


Figure 21 b Distillation Curves for Gasoline and Ethanol Gasoline Blends (144)

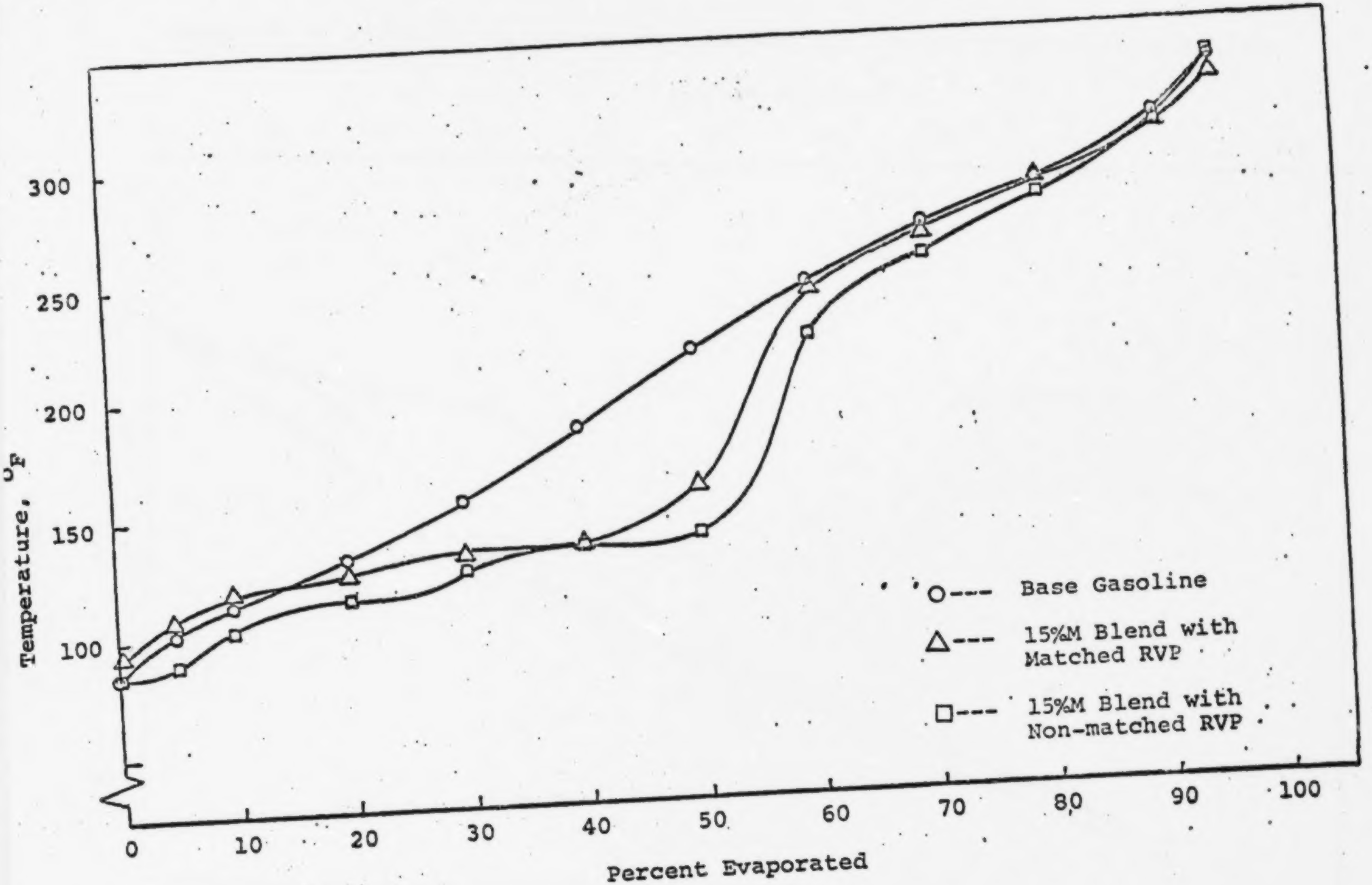


Figure 22 a Distillation Curves for Gasoline and Methanol Blends (187)

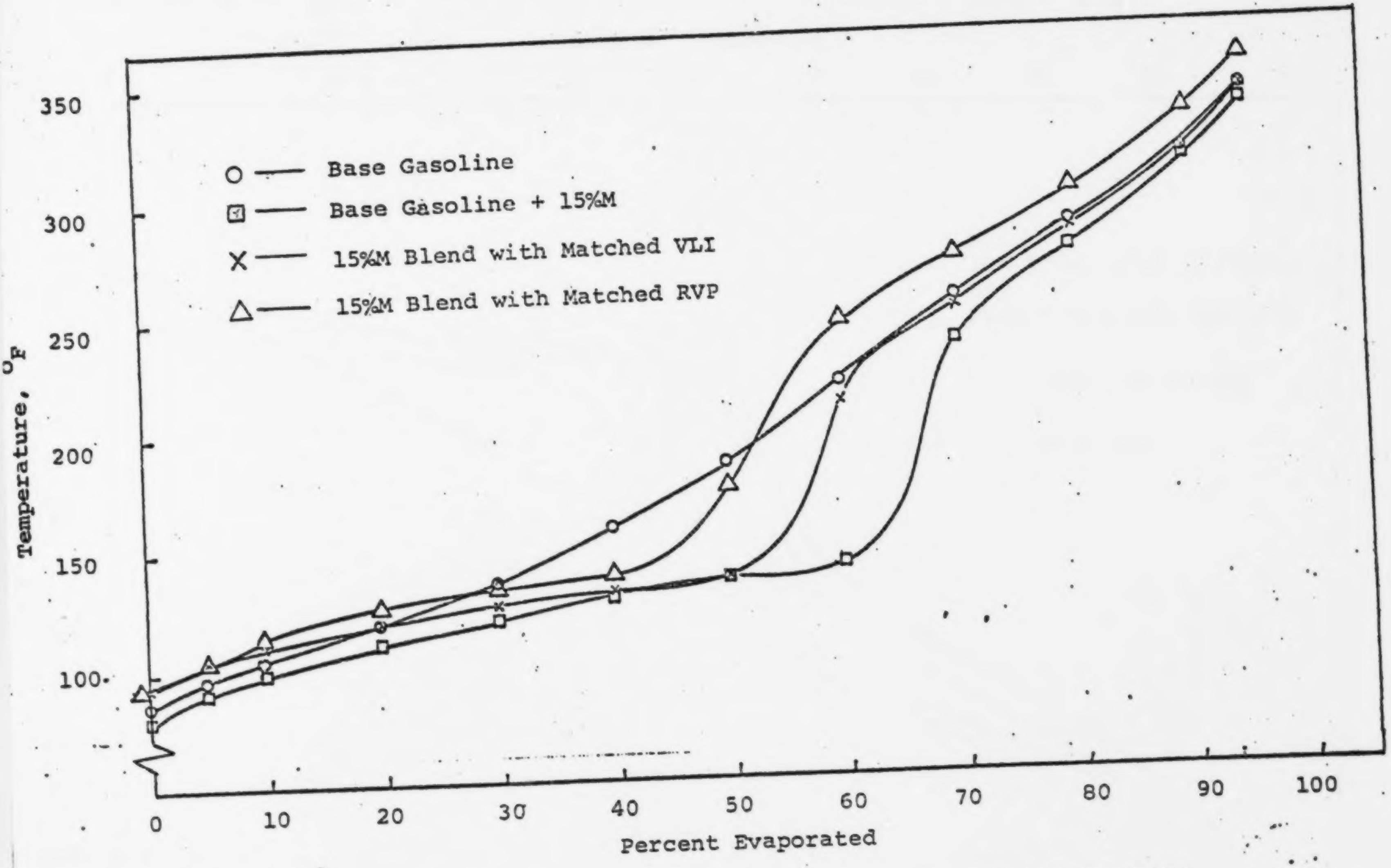


Figure 22 b Distillation Curves for Gasoline and Methanol Blends (187)

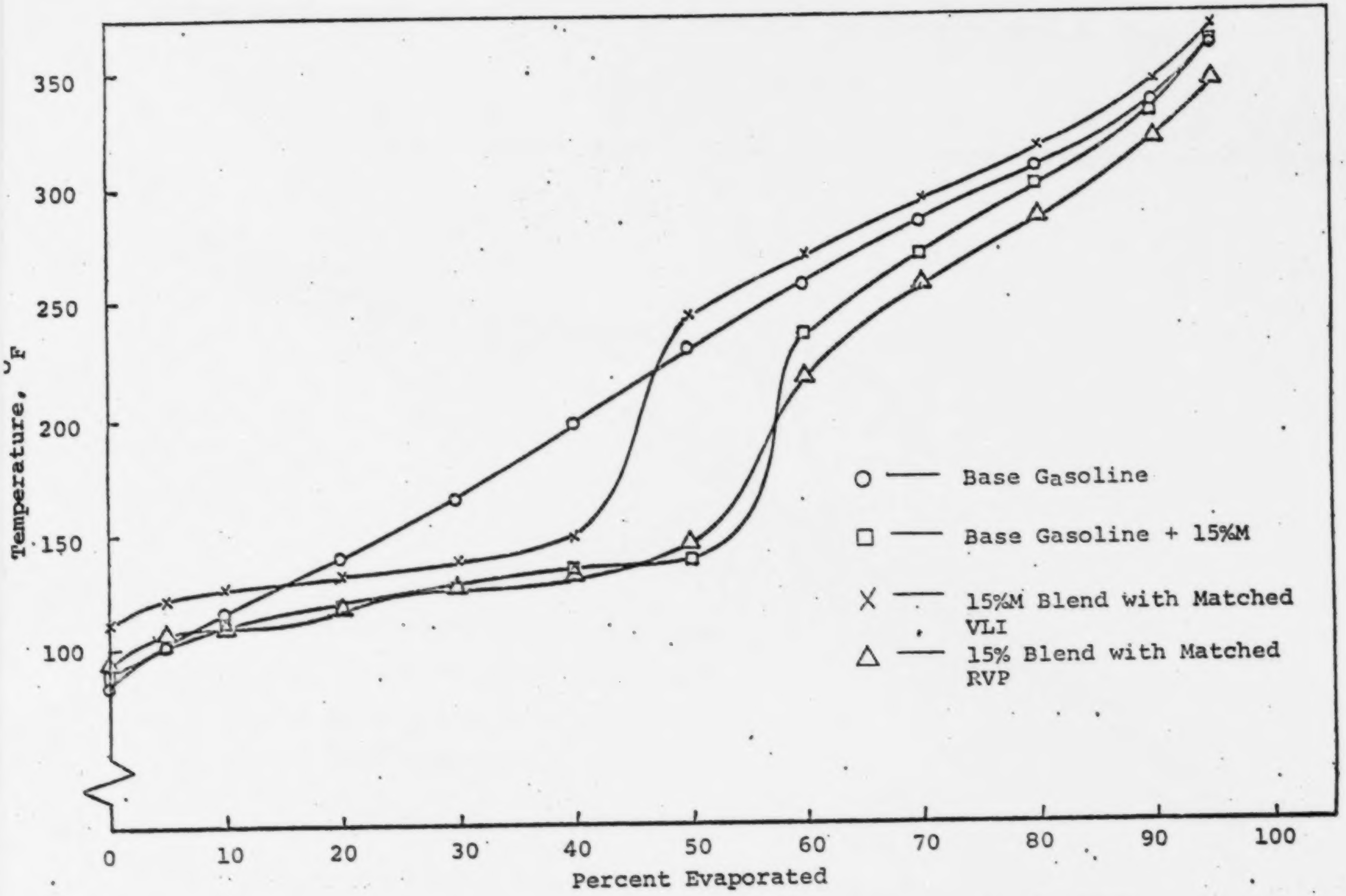
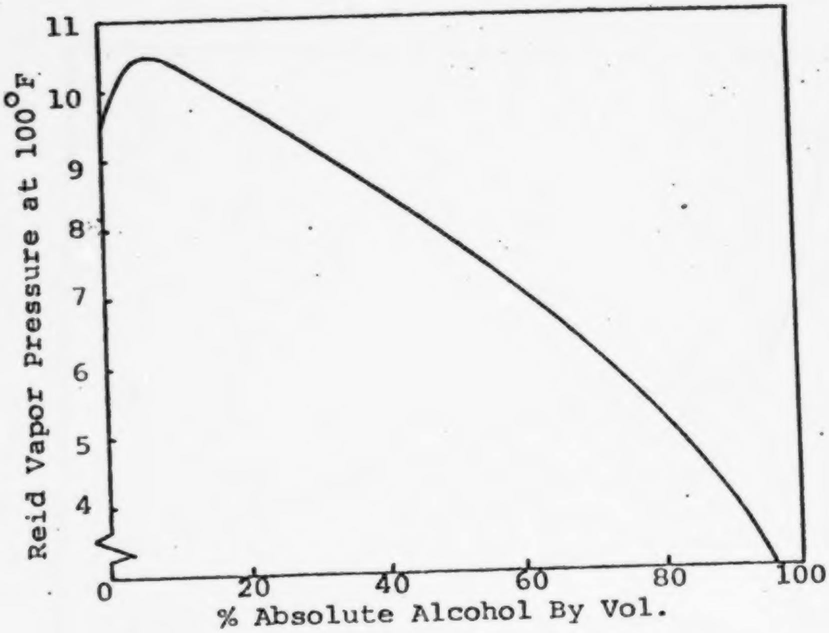
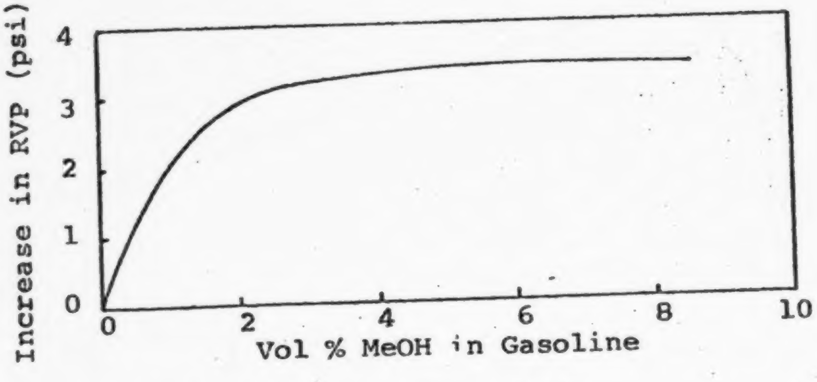


Figure 22 c Distillation Curves for Gasoline and Methanol Blends (187)



a.) Ethanol blends (32)



b.) Methanol blends (187)

Figure 23 Reid Vapor Pressure for Alcohol-Gasoline Blends

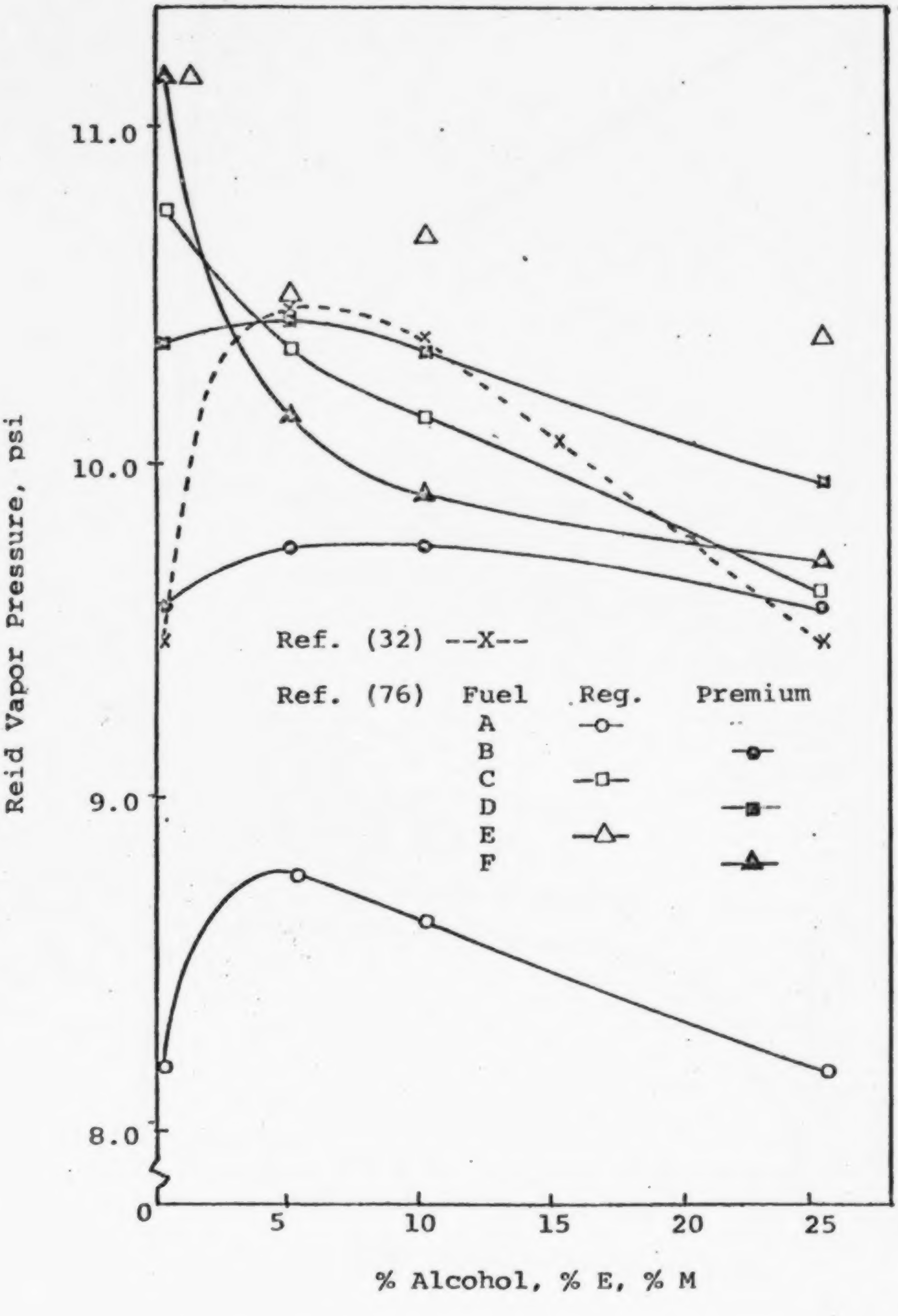


Figure 24 Reid Vapor Pressure for Ethanol Blends

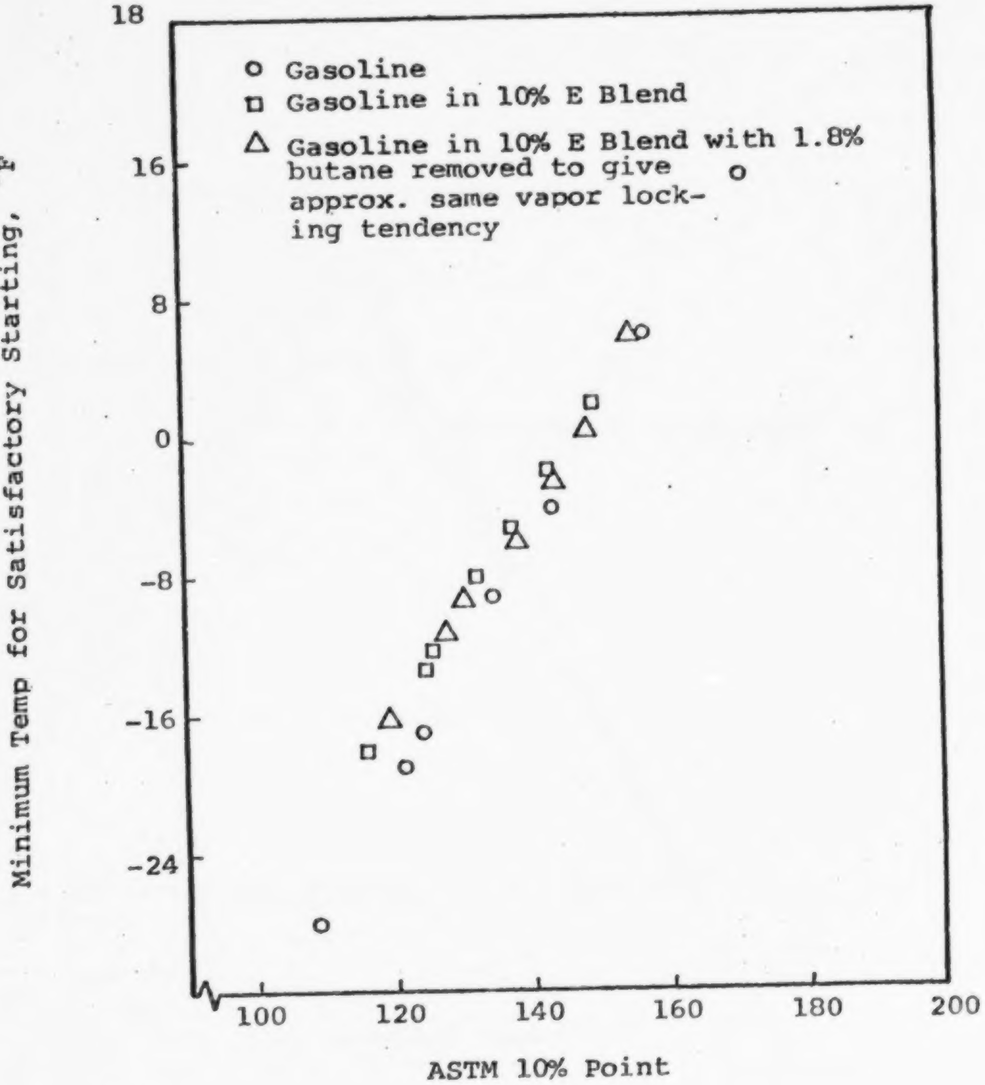


Figure 25 ASTM 10% Point and Cold Start Correlation for Ethanol Blends (29)

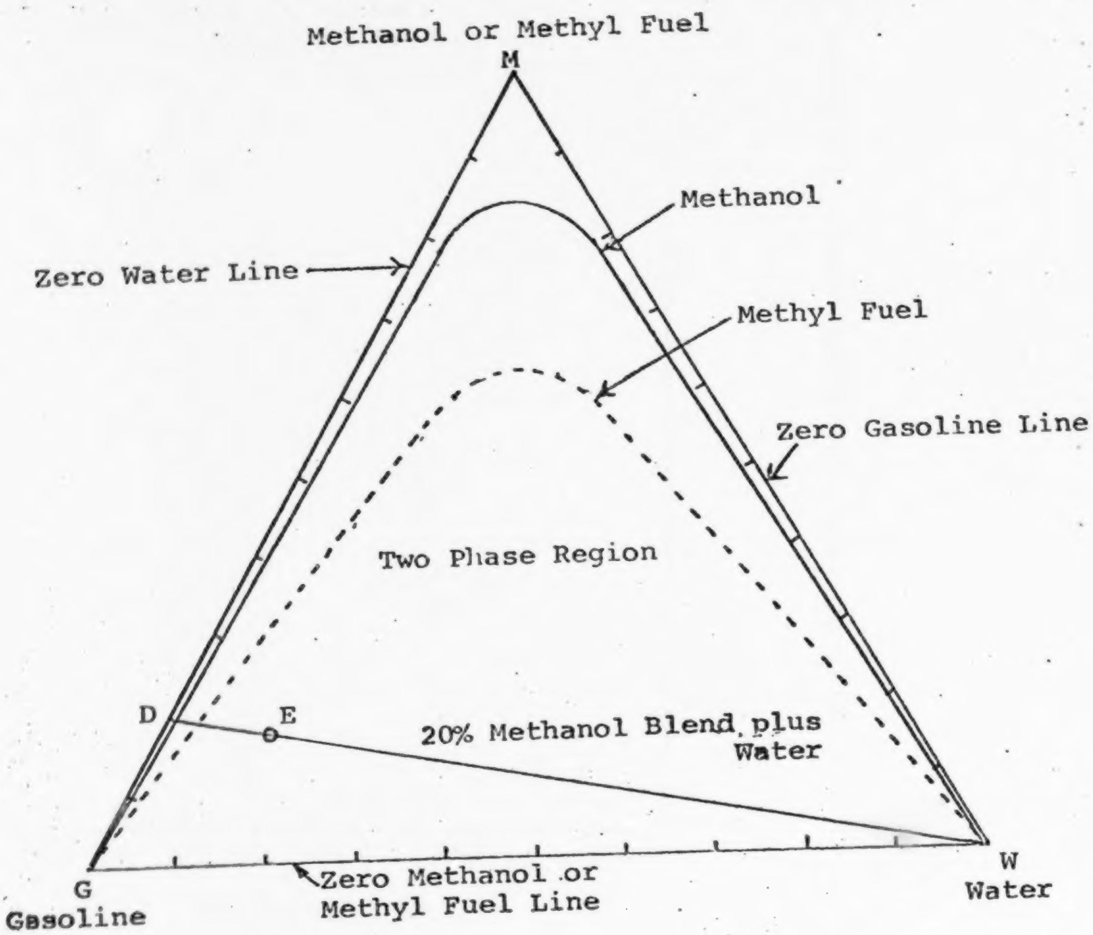


Figure 26 Equilibrium Phase Diagram For Methanol or Methyl Fuel, Gasoline and Water Based on Volume % (176)

APPENDIX A

EXHAUST MASS EMISSIONS RELATIONSHIPS

In this Appendix relationships are derived which allow one to determine exhaust gas mass emissions from exhaust species molar concentration and fuel consumption measurements for methanol-gasoline blends.

The combusion of one mole of a fuel blend composed of f moles of methanol (CH_3OH) and (1-f) moles of hydrocarbon C_XH_Y with air may be expressed in the following form:

$$
\begin{aligned}
&(1-f)\ C_XH_Y + (f)\ CH_3OH + (n)\ O_2 + (3.76n)\ N_2 \rightarrow \\
&(a)\ CO_2 + [(1-f)\ X + f - Ac - a-e-k]CO + (c)\ C_A\ H_B \\
&+ (b)\ H_2O + (d)\ NO_x + [(1-f)y/2 + 2f - cB/2-b-e-2k]\ H_2 \\
&+ (f/2 + n - a - [(1-f)\ X + f - Ac - a-e-k]/2-b/2-dx/2-e/2-k/2]O_2 \\
&+ (3.76n - d/2)\ N_2 + (e)\ HCHO + (k)\ CH_3OH. \qquad (A1)
\end{aligned}
$$

For generality the unburned hydrocarbon in the exhaust is expressed as C_AH_B and the oxides of nitrogen as NO_X. Exhaust alcohol is considered to be methanol and exhaust aldehyde to be formaldehyde.

Exhaust Hydrocarbons - The number of moles of unburned hydrocarbon produced per mole of fuel blend consumed is:

$$\frac{\text{mole } C_AH_B}{\text{mole fuel blend}} = c\ . \qquad (A2)$$

Conservation of carbon atoms in Equation (A1) yields the following relationship:

$$(1-f)X + f = a + [(1-f)X + f - Ac - a-e-k] + Ac + e + k \qquad (A3)$$

which, when combined with Equation (A2), yields:

$$\frac{\text{mole } C_AH_B}{\text{mole fuel blend}} = \frac{c\ [(1-f)\ X + f\ ]}{a + [(1-f)X + f - Ac-a-e-k] + Ac + e+k} . \qquad (A4)$$

If it is assumed that the products of combustion can be treated as a perfect gas (excluding any condensed water) the mole fraction of each exhaust species is equal to its volume fraction (or volume percent or ppm by volume). Thus, Equation (A4) can be rewritten in terms of (i) which is defined as the percent of species i per unit volume as follows:

$$\frac{\text{mole } C_AH_B}{\text{mole fuel blend}} = \frac{(C_AH_B)\ [(1-f)X + f\ ]}{(CO_2) + (CO) + A\ (C_AH_B) + (HCHO) + (CH_3OH)} . \tag{A5}$$

The molecular weight of the unburned exhaust gas hydrocarbon is

$$M_{C_AH_B} = 12\ A + B \tag{A6}$$

and the molecular weight of the fuel blend is:

$$M_{blend} = (1 - f)\ (12X+Y) + 32f \tag{A7}$$

where the molecular weights of carbon, hydrogen and oxygen are taken to be 12, 1 and 16 respectively. Combination of Equations (A5), (A6) and (A7) yields the following expression for the ratio of mass of C_AH_B produced per mass of fuel blend:

$$\frac{\text{mass } C_AH_B}{\text{mass fuel blend}} = \frac{(12A+B)}{[(1-f)\ (12X+Y)+32f]}\ \frac{(C_AH_B)\ [(1-f)\ X+f]}{[(CO_2) + (CO) + A\ (C_AH_B) + (HCHO) + (CH_3OH)\ ]} . \tag{A8}$$

If the total hydrocarbon content in the exhaust is expressed in terms of equivalent carbon content such as is measured with a flame ionization detector (FID) then for a (FID) calibration gas (neglecting differences in FID relative hydrocarbon response) C_pH_q

$$A\ (C_AH_B) = p\ (C_pH_q) \tag{A9}$$

Substitution of Equation (A9) into (A8) yields:

$$\frac{\text{mass } C_AH_B}{\text{mass fuel blend}} = \frac{(12+B/A)\ [(1-f)X+f]}{(1-f)\ (12X+Y)\ +32f}\ \frac{p(C_pH_q)}{(CO_2) + (CO) + p(C_pH_q) + (HCHO) + (CH_3OH)} . \tag{A10}$$

Equation (A10) can be used to determine the mass emission of C_AH_B produced per unit mass of fuel blend consumed, provided the volume percentages (or ppm or concentration) of CO_2, CO, equivalent C_pH_q, HCHO, and CH_3OH are measured and the fuel composition X, Y and f are known. In practice, the terms $p(C_pH_q)$, (HCHO) and (CH_3OH) are small compared to (CO_2) and (CO).

When a mixture of hydrocarbons such as Indolene is used as fuel representative of gasoline, $f = 0$ and the average fuel molecule C_xH_y can be approximated by $X = 7$ and $Y = 13.02$. The equivalent carbon content $p(C_pH_q)$ can be measured with a flame ionization detector (FID). When Indolene/methanol blends are used problems arise in using the FID in that the response of the FID to methanol is suspected of being low, and corrections must be made to the FID output.

During experiments, blends of methanol and Indolene can be made either on a mass or volume base. The mass fraction of methanol in the blend, mf, and the volume fraction of methanol in the blend, vf, are related to the mole fraction, f, as follows: a mole of blend containing f mole fraction of methanol is represented by the chemical formula:

$$\text{mole blend} = (1-f)\ C_XH_Y + f\ CH_4O. \qquad \text{(A11)}$$

The corresponding mass of the mole of blend, m, is

$$m = (1-f)\ (12X+Y) + 32f, \qquad \text{(A12)}$$

and the mass fraction of methanol in the blend is thus

$$mf = \frac{32f}{(1-f)\ (12\ X+Y) + 32f} \qquad \text{(A13)}$$

From Equation (A13) the mole fraction is related to the mass fraction as follows:

$$f = \frac{mf \quad (12X+Y)}{mf \quad (-32+12X+Y) + 32} . \qquad \text{(A14)}$$

If a volume of blend is formed by mixing vf volume units of methanol and (1-vf) volume units of C_XH_Y then the mole fraction, f, in Equation (A10) is related to the volume of methanol, vf, as follows: the mass of the blend is

$$m = \rho_{CH_3OH} \, vf + \rho_{C_XH_Y} (1-vf), \qquad \text{(A15)}$$

where ρ_i is the mass of blend component i per unit volume. The mass fraction of methanol is thus

$$mf = \frac{\rho_{CH_3OH} \, vf}{\rho_{CH_3OH} vf + \rho_{C_XH_Y} (1-vf)} , \qquad \text{(A16)}$$

In terms of specific gravity (sg) the above equation becomes

$$mf = \frac{vf}{vf + \frac{(sg)_{C_XH_Y}}{(sg)_{CH_3OH}} (1-vf)} . \qquad \text{(A17)}$$

Equation (A14) can be used in conjunction with (A17) to determine the mole fraction in terms of volume fraction.

Exhaust Carbon Monoxide - The expression, corresponding to Equation (A4), relating the molar production of carbon monoxide to molar fuel consumption is

$$\frac{\text{moles CO}}{\text{mole fuel blend}} = \frac{Z \, [(1-f) \; X + f]}{a + Z + Ac + e + k} , \qquad \text{(A18)}$$

where

$$Z = (1-f)X + f - Ac - a - e - k . \qquad \text{(A19)}$$

In terms of (i) Equation (A18) becomes

$$\frac{\text{moles CO}}{\text{mole fuel blend}} = \frac{(CO)\,[(1-f)X + f]}{(CO_2) + (CO) + A(C_AH_B) + (HCHO) + (CH_3OH)} \quad \text{(A20)}$$

Equation (A20) can be expressed in terms of mass as follows:

$$\frac{\text{mass CO}}{\text{mass fuel blend}} = \frac{28}{(1-f)\,(12X+Y) + 32f}\;\frac{(CO)\,[(1-f)X+f]}{(CO_2) + (CO) + p(C_pH_q) + (HCHO) + (CH_3OH)} \quad \text{(A21)}$$

Exhaust Nitric Oxide - The expression, corresponding to Equation (A4), relating the molar production of Nitric Oxide to molar fuel consumption is

$$\frac{\text{moles }NO_x}{\text{mole fuel blend}} = \frac{d\,[(1-f)X+f]}{a + Z + Ac + e + k} \quad \text{(A22)}$$

In terms of (i) Equation (A22) becomes

$$\frac{\text{moles }NO_x}{\text{mole fuel blend}} = \frac{(NO_x)\,[(1-f)\,X+f]}{(CO_2) + (CO) + A(C_AH_B) + (HCHO) + (CH_3OH)} \quad \text{(A23)}$$

In terms of mass production Equation (A23) becomes

$$\frac{\text{mass }NO_x}{\text{mass fuel blend}} = \frac{(14+16x)}{(1-f)\,(12X+Y) + 32f}\;\frac{(NO_x)\,[(1-f)X+f]}{(CO_2) + (CO) + p(C_pH_q) + (HCHO) + (CH_3OH)} \quad \text{(A24)}$$

where the molecular weight of nitrogen is taken to be 14. From Equation (A24) nitric oxide mass emissions may be expressed as either NO or, as is specified in the Federal Text Procedures, as NO_2.

APPENDIX B - MIXTURE TEMPERATURE CALCULATIONS

Mixture Temperature - In order to estimate the temperature drop in going from a stoichiometric mixture of air and liquid fuel to one of air and vaporized fuel in an adiabatic process, the first law of thermodynamics is applied to the control volume shown on the next page. Such an application yields the following equation:

$$\dot{m}_f\,(h_{f2} - h_{f1}) + \dot{m}_a\,(h_{a2} - h_{a1}) = 0, \qquad \text{(B1)}$$

where $\dot{m}$ is mass flow rate; h is enthalpy; f is fuel; a is air; and 1 and 2 designate the entrance and exit conditions respectively. The enthalpy of the fuel-air mixture is assumed to be the enthalpies of the mixture's constituents. Assuming constant specific heat for the fuel vapor, the following relationship can be written:

$$h_{f2} - h_{f1} = h_{lv} + C_{pf}(T_2 - T_1), \qquad \text{(B2)}$$

where h_{lv} is the difference between the enthalpy of vapor fuel and liquid fuel at the temperature T_1 (latent heat of vaporization @ T_1); C_{pf} is the specific heat at constant pressure of the fuel vapor; and T_2 and T_1 are the exit and inlet temperatures respectively. Assuming constant specific heat for air the following relationship can be written:

$$h_{a2} - h_{a1} = C_{pa}\,(T_2 - T_1). \qquad \text{(B3)}$$

Equations (B1), (B2) and (B3) can be combined to yield

$$T_1 - T_2 = \frac{h_{lv}\,\dfrac{\dot{m}_f}{\dot{m}_a}}{\dfrac{\dot{m}_f}{\dot{m}_a}\,C_{pf} + C_{pa}} \qquad \text{(B4)}$$

Letting ΔT represent the temperature drop $(T_1 - T_2)$ and replacing $\dot{m}_a/\dot{m}_f$ with the symbol for air-fuel ratio (AF) Equation (B4) becomes

$$\Delta T = \frac{\dfrac{h_{lv}}{(AF)}}{C_{pa} + \dfrac{C_{pf}}{(AF)}} \qquad \text{(B5)}$$

Substitution of stoichiometric air-fuel ratios and the other properties listed in the following table yields the values of the temperature drop presented in Section II. A-1.

	$h_{lv}\ \frac{BTU}{lbm}^*$	$c_{pa}\ \frac{BTU}{lbm\ ^oF}$	$c_{pf}\ \frac{BTU}{lbm\ ^oF}$	AF	$\Delta T\ ^oF$
Gasoline	150	0.24	0.50	14.9	37
Methanol	474	0.24	0.38	6.45	246
Ethanol	364	0.24	0.38	9.01	143

*Property values taken from References (87 , and 115).

According to Reference (127), the vapor pressure of methanol, P mm hg, corresponding to the temperature T, °K, is given by the following equation:

$$\text{Log}_{10}\ P = -\frac{1961.9}{T} + 8.6398 \qquad \text{(B6)}$$

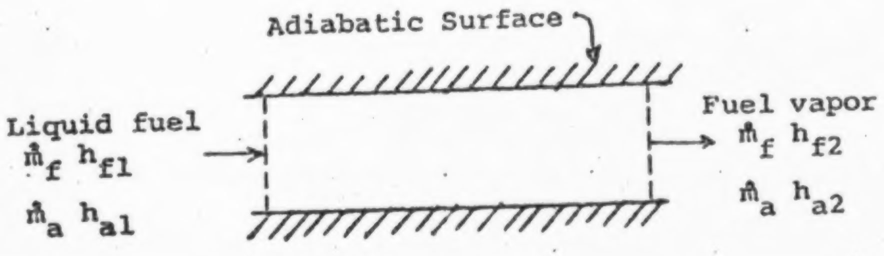
A stoichiometric mixture of air and vaporized methanol contains 1 volume unit of methanol per 8.15 volume units of mixture according to the following chemical equation for complete combustion:

$$CH_3OH + 1.5\ O_2 + 5.65\ N_2 \rightarrow CO_2 + 2H_2O + 5.65\ N_2\ . \qquad \text{(B7)}$$

Thus, assuming ideal gas behavior the partial pressure of methanol in such a mixture is

$$P_M = 0.123\ P_T\ , \qquad \text{(B8)}$$

where P_T is the total pressure of the mixture. For wide open throttle condition ($P_T \approx 760$ mm hg) the partial pressure of methanol in a stoichiometric air-vaporized fuel mixture is thus $P_M \approx$ 93 mm hg. From Equation (B6) the corresponding saturation temperature is 70°F as presented in Section II. A-1.



APPENDIX C - BLEND STOICHIOMETRY

In this Appendix the Equations which were used to generate curves of stoichiometric air-fuel ratio for the various alcohol-hydrocarbon blends presented in Figure 18 are developed.

Methanol-Isooctane Blends - For stoichiometric and complete combustion of a blend containing f moles of methanol and 1-f moles of isooctane the following chemical equation applies:

$$(1-f)\ C_8H_{18} + f\ CH_3OH + (12.5 - 11f)\ O_2 + (12.5 - 11f)\ 3.76N_2$$
$$\rightarrow (8(1-f) + f)\ CO_2 + \tfrac{1}{2}\ (1-f)\ 18 + 4f)\ H_2O + (12.5 - 11f)\ 3.76N_2. \quad (C1)$$

From Equation (C1) the AF ratio can be calculated as a function of f:

$$AF = \frac{(12.5 - 11f)\ 32 + (12.5 - 11f)\ (3.76)\ 28}{(8)(12)\ (1-f) + 18\ (1-f) + 12f + 4f + 16f}, \quad (C2)$$

$$AF = \frac{1716 - 1510f}{114 - 82\ f}. \quad (C3)$$

Instead of mole fraction it is more useful to express the AF ratio in terms of % M. To do this the following relations are needed: Equation (A14) with X = 8 and Y = 18 yields the following relationship between the mass fraction mf and the mole fraction f:

$$f = \frac{114\ mf}{82\ mf + 32}. \quad (C4)$$

On substituting the specific gravities of 0.796 for methanol and 0.696 for isooctane Equation (A17) yields the following relationship between mass fraction mf and volume fraction Vf (or % M/100) of methanol in the blend:

$$mf = \frac{Vf}{Vf + 0.874\ (1-vf)} = \frac{\%\ M/100}{\%M/100 + (0.874)\ (1-\%M/100)}. \quad (C5)$$

Methanol-Indolene Blends. The expression corresponding to Equations (C1), (C3), (C4), and (C5) for Methanol-Indolene blends are (C6), (C7), (C8), and (C9) respectively as presented below.

$$(1-f)\ C_7H_{13.02} + f\ CH_3OH + (10.255-8.755f)\ O_2 + (10.255-8.71f)\ 3.76N_2$$
$$\rightarrow (7-6f)\ CO_2 + \tfrac{1}{2}\ (13.02 - 9.02f)\ H_2O + (10.255-8.71f)\ 3.76N_2 \qquad (C6)$$

$$AF = \frac{1407.81 - 1201.89f}{97.02 - 65.02f} \qquad (C7)$$

$$f = \frac{97.02\ mf}{65.02mf + 32} \qquad (C8)$$

$$mf = \frac{vf}{vf + 0.93\ (1-vf)} = \frac{\%M/100}{\%M/100 + 0.93\ (1-\%M/100)}\ . \qquad (C9)$$

In Equation (C9) the specific gravity of Indolene is taken to be 0.74.

Ethanol-Isooctane Blends. The expressions corresponding to Equations (C1), (C3), (C 4) and (C5) for Ethanol-Isooctane blends are (C10), (C11), (C12) and (C13) respectively as presented below.

$$(1-f)\ C_8H_{18} + f\ C_2H_5OH + (12.5 - 9.5f)\ O_2 + (12.5 - 9.5f)\ 3.76N_2$$
$$\rightarrow (8(1-f) + 2f)\ CO_2 + \tfrac{1}{2}\ ((1-e)\ 18 + 6f)\ H_2O + (12.5-9.5f)\ 3.76N_2 \qquad (C10)$$

$$AF = \frac{1716 - 1304\ f}{114 - 68f} \qquad (C11)$$

$$f = \frac{114\ mf}{68\ mf + 46} \qquad (C12)$$

$$mf = \frac{vf}{vf + 0.887\ (1 - vf)} = \frac{\%E/100}{\%E/100 + 0.887\ (1-\%E/100)}\ . \qquad (C13)$$

In Equation (C13) the specific gravity of ethanol is 0.785.

APPENDIX D - BLEND-LEANING EFFECT. In order to estimate the change in equivalence ratio that occurs when a methanol blend is substituted for gasoline, it is assumed that the carburetor discharge coefficient, C_D, is the same for isooctane and the methanol blend for a given air-flow rate. As reported by Bolt et al.(123) this is not necessarily the case but it at least gives a first order approximation.

The carburetor throat pressure for a given air-flow will be the same at a specified air-flow rate for both fuels and thus the mass flow for the fuels is related by Equation (D1)

$$\frac{\dot{m}_B}{\dot{m}_G} = \sqrt{\frac{\gamma_B}{\gamma_G}} \qquad \text{(D1)}$$

when the assumption of equal discharge coefficient is invoked (123).

The specific gravity ratio appearing in Equation (D1) is related to the mass fraction, m_f, of methanol in the blend as follows, and is plotted in Figure 20.

$$\frac{\gamma_B}{\gamma_G} = \frac{(mf)_M \ \gamma_M + (1- (mf)_M) \ \gamma_G}{\gamma_G} . \qquad \text{(D2)}$$

The mass fraction in turn is related to the volume fraction vf or % M according to the following equation which is taken from Appendix A, Equation (A17):

$$m_f = \frac{vf}{vf + \frac{\gamma_G}{\gamma_M} (1-vf)} . \qquad \text{(D3)}$$

In Figure 3 the relation between mass fraction and volume fraction is plotted for a blend comprised of methanol and gasoline with a specific gravity of 0.74.

For a 20% M blend (vf = 0.2) Figure 3 yields mf = 0.212. With mf = 0.212, Equations (D1) and (D2) yield the following as the ratio of 20% M blend fuel flow to 0.74 specific gravity gasoline fuel flow at equal air-flow:

$$\frac{\dot{m}_{20\%\ M}}{\dot{m}_{Gasoline}} = 1.008 \quad . \tag{D4}$$

Thus, there is a slight 0.8% increase in fuel flow delivered by the carburetor when the 20% M blend is substituted for gasoline. To maintain equal stoichiometry, however, it is necessary to increase the fuel flow by a greater amount. Appendix C contains calculations for the required change in air-fuel ratio when an alcohol blend is substituted for isooctane or Indolene. The results are presented in Figure 18. Figure 18 shows that when a 20% methanol-Indolene blend is substituted for Indolene the air-fuel ratio must decrease from 14.5 to 12.8 if an equivalence ratio of unity is to be maintained. As seen above, in the carburetor calculations, the blend fuel flow increases by only 0.8%. Thus, the resulting air-fuel ratio delivered by the unmodified carburetor with the 20% M-Indolene blend is 14.5/1.008 or 14.4. Hence, the equivalence ratio for the 20% M-Indolene blend is 12.8/14.4 or 0.88. The decrease in Φ is thus 0.12 units as discussed in Section II. A-3, "Blend Leaning Effect."

Calculations similar to the above have been made for 0 to 100% methanol-Indolene blends. The blend-leaning effects thus calculated are presented in Figure 11.

APPENDIX E

OUTLINES OF VARIOUS REFERENCES

During the course of the evaluation of past and current studies it was found convenient to summarize and outline various reference articles. This Appendix contains these outlines. They are presented in the order in which they appear in the Bibliography Section. Only a portion of the Bibliography entries are outlined. The omission of an entry from the outline is in no way related to its importance. Some of the more significant works have not been included because they were not made available soon enough for proper outlining and typing.

It should be pointed out that the results contained in this Appendix should not be used without consulting the original work for it was not possible to list all of the conditions, assumptions, and test procedures used in the original work. To use the results presented without consulting the original would be equivalent, in most instances, to taking them out of context.

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Bridgeman,O.C. and Querfeld, D., (16).
SOLUBILITY OF ETHYL ALCOHOL IN GASOLINE
Industrial and Engineering Chemistry Vol. 25, May, 1933

and

CRITICAL SOLUTION TEMPERATURES OF MIXTURES OF GASOLINE, ETHYL ALCOHOL, AND WATER
Bureau of Standards Journal of Research. Vol.10, March 1933

Critical solution temperatures were obtained for 23 gasolines (Table 1) with 10 to 90%(v) ethanol and 1.13 to 8.27%(v) H_2O.* Typical data shown below.

TABLE I. IDENTIFICATION DATA ON GASOLINES

GASOLINE	SOURCE	EVAPORATION TEMPERATURE 10% °C.	50% °C.	90% °C.	d^{20}_{4}
1	Pennsylvania	70	135	199	0.738
2	Kansas	70	106	152	0.734
3	California	66	108	151	0.730
4	Oklahoma	72	124	191	0.739
5	California	58	110	156	0.732
6	East Texas	58	110	162	0.723
7	Cracked	54	120	188	0.731
8	Cracked	60	142	191	0.773
9	Topped No. 1	60	107	153	0.720
10	Topped No. 7	54	96	150	0.722
11	Topped No. 8	60	102	153	0.731
12	Commercial	61	130	183	0.742
13	Commercial	58	123	181	0.742
14	Commercial	68	127	175	0.713
15	Commercial	60	136	186	0.752
16	Commercial	65	124	174	0.741
17	Commercial	60	131	187	0.752
18	No. 1 + 10% pentane	64	128	197	0.731
19	No. 1 + 20% pentane	55	119	196	0.721
20	No. 1 + 30% pentane	42	104	192	0.707
21	No. 1 + 10% California natural gasoline	60	128	197	0.736
22	No. 1 + 20% California natural gasoline	61	120	195	0.727
23	No. 1 + 30% California natural gasoline	57	111	193	0.710

TABLE II. CONCENTRATION OF ETHYL ALCOHOL SOLUTIONS

SAMPLE	d^{60}_{60}	ALCOHOL AT 60° F. (15.6° C.) Vol. %	WATER AT 60° F. (15.6° C.) Vol. %
A	0.79820	99.13	1.13
B	0.80205	98.33	2.14
C	0.80581	97.49	3.18
D	0.80931	96.67	4.18
E	0.81275	95.83	5.19
F	0.81619	94.96	6.22
G	0.81948	94.09	7.25
H	0.82275	93.21	8.27

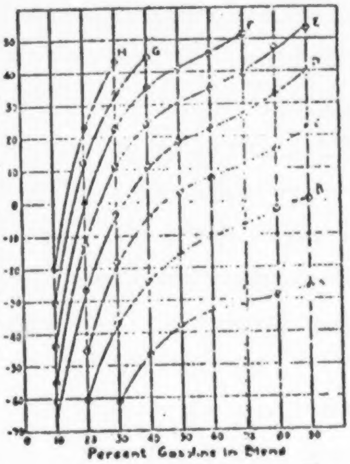

FIGURE 2. CRITICAL SOLUTION TEMPERATURES OF BLENDS OF ETHYL ALCOHOL AND GASOLINE 1

At each constant percentage of gasoline in the blend, it w found that the logarithm of the percentage, s, of water pa was a linear function of the reciprocal of the critical solu temperature, T, in absolute Centigrade degrees, so that

$$\log s = a + \frac{b}{T}$$

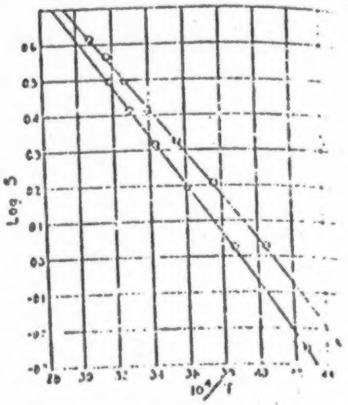

FIGURE 5. METHOD OF PLOTTING E PERIMENTAL DATA FOR INTERPOLATI PURPOSES

Logarithm of percentage of water in ble plotted against reciprocal of critical s temperature in ° K.

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* The percentage of gasoline in the blend is the volume of gasoline at 60°F., which, when added to the appropriate volume of alcohol solution, gives a summation of volumes equal to 100.. Volume per cent refers to the volume of alcohol (or of water, respectively) at 60°F.(15.6°C.) in 100 ml. of solution at 60°F.

DISCUSSION OF RESULTS

1."The critical solution temperature decreases markedly as the concentration of water in the alcohol solution decreases and as the percentage of gasoline in the blend decreases.

2. For straight-run fuels of the same volatility, the critical solution temperatures differ little from fuel to fuel. Cracked gasolines may, however, show much lower crtical solution temperatures than straight-run products even of the same volatility.

3. With the exception of cracked gasolines 10 and 11, none of the gasolines studied would give sufficiently low critical solution temperatures to make practical the use in freezing temperatures of blended fuels containing up to 50 per cent alcohol unless the alcohol was almost entirely free from water, for some margin of safety must be provided for absorption of moisture after blending."

Bridgeman, O.C. (National Bureau of Standards), (29).
UTILIZATION OF ETHANOL-GASOLINE BLENDS AS MOTOR FUEL
Industrial and Engineering Chemistry, Vol. 28, No.9, Sept. 1936

PERFORMANCE AND FUEL CONSUMPTION Based on a survey of published anhydrous ethanol blend data Bridgeman concludes:

1) "When used in the same engine, particularly with the carburetor and spark set for the mean of the optimum values for the two types of fuels, little difference in power, acceleration, or fuel consumption is observed with a 10% blend or even under many operating conditions with a 20% blend. Satisfactory engine performance could not be obtained with a 40% blend and gasoline in the same engine with any fixed carburetor setting.

2) When used in the same engine, with carburetor and spark accurately adjusted to the optimum settings for each type of fuel, the same power and acceleration may be obtained at the expense of about 3 to 4% greater fuel consumption with a 10% blend, about double this difference with a 20% blend, and still more with a 40% blend.

3) Assuming that it is possible to produce and utilize gasoline having any desired octane number, the engine performance per gallon of fuel consumed will always be poorer with a blend of ethyl alcohol, when both fuels are used in the same engine."

VAPOR LOCK For the same freedom from vapor lock the RVP of a 10%E blend should be about 1 psi lower than that considered permissible for the gasoline (Figure to right) The RVP of gasoline increases about 0.8 psi with 10%E. Thus the gasoline used for blending should have a RVP 1.8 psi lower than that normally used. The increase in RVP for 20% blends is 0.5 psi and for 40% blends a decrease of 0.5psi. Conclusions regarding vapor lock are:

1."When used in the same engine, a 10% alcohol blend is more likely to give trouble from vapor lock than the gasoline with which the alcohol is blended. Little difference would be expected with a 20% blend, and the situation would be reversed with a 40% blend, since there is greater freedom from vapor lock difficulties with the blend than with the gasoline from which the 40% blend was prepared.

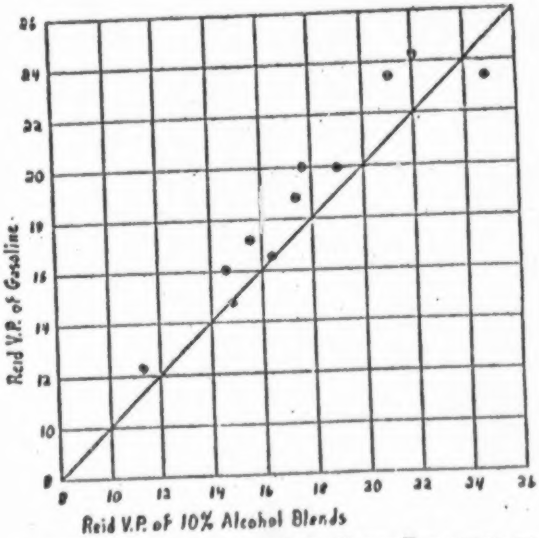


Figure 2. Comparison of Reid Vapor Pressures of Gasolines and 10 Per Cent Alcohol Blends Which Caused Vapor Lock in Eleven Makes of Cars at 40 mph.

2. The same freedom from vapor lock may be obtained for a 10% blend and gasoline if the vapor pressure of the gasoline used for blending is lower than that of the gasoline with which the blend is compared. In this case there is some loss in octane number due to use of less butane, and there is increased difficulty in engine starting. On the other hand, with a 40% blend a gasoline of increased vapor pressure may be employed with enhancement of the octane number above that obtained by blending with alcohol."

ENGINE STARTING

1. "When comparing gasolines and the same gasolines with 10% ethyl alcohol, engine starting will be easier with the blend at temperatures above 0°F. and will be more difficult with the blend at temperatures below-10°F., with little difference in the intermediate range. The conclusions are not changed when the blend has the same vapor-locking tendency as the gasoline. Greater difficulties in engine starting would be experienced with 20% blends and in particular with 40% blends.

2. The same ease of engine starting at low temperatures can be obtained by using more volatile gasolines for blending, but this requires improvement in the fuel feed systems in order to eliminate the increased vapor-locking tendency of such blends.

3. In starting at temperatures above 0°F., the 10% blend will permit starting with lower fuel consumption, whereas the reverse is true at lower temperatures."

WATER TOLERANCE

TABLE VI. WATER TOLERANCES OF BLENDS OF ETHYL ALCOHOL AND AN AVERAGE COMMERCIAL GASOLINE

	Water Tolerance, Vol. %			
Temp., °F.	5% blend	10% blend	20% blend	40% blend
104	0.10	0.46	1.11	2.70
68	0.15	0.35	0.83	2.03
32	0.11	0.25	0.59	1.46
−4	0.07	0.18	0.40	1.00
−40	0.05	0.11	0.26	0.64

Not feasible to employ 95% ethanol for blending unless the blend was always used at temperatures considerably above freezing. By employing ethanol almost free from water, use of about 5% of one of the higher alcohols as a blending agent would probably permit car operation under most conditons without separation.

TABLE VIII. INCREASE IN WATER TOLERANCE PRODUCED BY ADDITION OF VARIOUS PERCENTAGES OF ISOPROPYL ALCOHOL TO BLENDS OF GASOLINE 26 WITH 5 AND 10 PER CENT OF ETHYL ALCOHOL

		Vol. % Water Tolerance for Stated Percentages of Isopropyl Alcohol Added to Blend:			
Temp., °F.	Ethyl Alcohol in Blend, %	0%	1%	3%	5%
104	5	0.20	0.26	0.38	0.51
	10	0.48	0.55	0.70	0.85
68	5	0.16	0.21	0.32	0.43
	10	0.38	0.44	0.58	0.72
32	5	0.13	0.17	0.26	0.36
	10	0.20	0.34	0.46	0.58
−4	5	0.09	0.13	0.20	0.29
	10	0.21	0.25	0.34	0.43
−40	5	0.06	0.09	0.15	0.22
	10	0.14	0.17	0.23	0.30

TABLE IX. INCREASE IN WATER TOLERANCE PRODUCED BY ADDITION OF 5 PER CENT OF VARIOUS HIGHER ALCOHOLS TO BLENDS OF GASOLINE 20 WITH 10 PER CENT OF ETHYL ALCOHOL

	Water Tolerance, Volume Per Cent					
Temp., °F.	No blending agent	n-Propyl	Iso-propyl	n-Butyl	Iso-butyl	tert-Butyl
104	0.48	0.90	0.85	0.92	0.90	0.86
68	0.38	0.75	0.72	0.80	0.77	0.73
32	0.29	0.61	0.58	0.67	0.64	0.60
−4	0.21	0.47	0.43	0.55	0.51	0.50
−40	0.14	0.35	0.30	0.43	0.39	0.39

CORROSION "Many instances of corrosion have been reported resulting for the most part from impurities in the blending agent employed, such as high amounts of sulfur in benzene or from corrosive acids formed on combustion (such as acetic acid) of some types of blending agents."

Christensen, L.M., (31)
ALCOHOL-GASOLINE BLENDS
Industrial and Engineering Chemistry, Vol. 28, No. 9, Sept. 1936

This paper is a literature survey of the use of ethanol gasoline blends. Information not presented in other summaries is given below.

WATER ABSORPTION of a 10%E blend is found to be dependent on the size of the container (surface to volume ratio). For a large commercial storage tank (50,000 gal.) the critical solution temperature is found to decrease over a 55 day period from -50°C to -55°C. This behavior is due to the distillation of an azeotropic ternary mixture of HC, H_2O and ethanol, resulting in dehydration of the stored blend. For a smaller volume the critical temperature was found to increase rather markedly.

PROPERTIES. The properties of ethanol and gasoline are in general not additive (see Figure to the right)

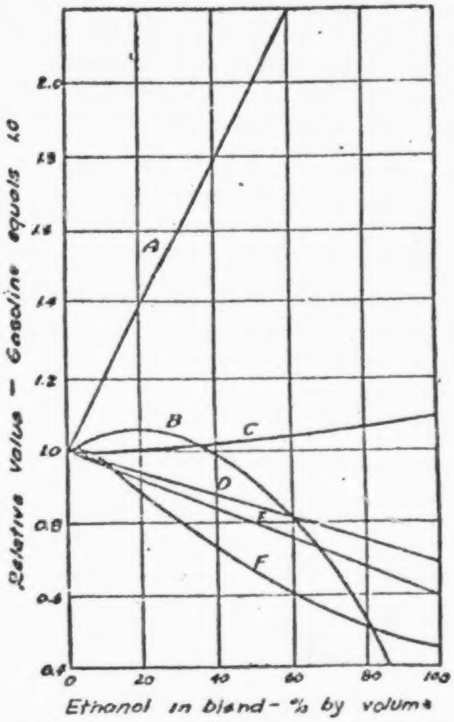


FIGURE 3. PHYSICAL-CHEMICAL PROPERTIES OF ALCOHOL-GASOLINE BLENDS

A. Latent heat of vaporization
B. Reid vapor pressure
C. Density
D. Heating value
E. Theoretical air-fuel ratio
F. Fluidity

MATERIALS COMPATIBILITY

1) Tests on various metals show that, except for tin, there is less corrosion by alcohol than gasoline.

2) 20%E blends showed no abnormal corrosion.

3) Both E and M react with M_g and Al at elevated temperatures.

4) Corrosion due to acetic acid formation might occur with fuels of very high alcohol content if certain metals, e.g., copper, were present in the combustion chamber.

PERFORMANCE The use of up to 25%E blends will result in no decrease in power or increase in sfc. Instead there may be a gain in power and lowering in sfc, especially when the engine is operated at part throttle with richer than maximum economy mixture.

Egloff, G. and Morrell, J.C., (32).
ALCOHOL-GASOLINE AS MOTOR FUEL
Industrial Engineering Chemistry, Vol. 28, No.9, Sept. 1936

This paper is a good 1936 literature survey of ethanol blends. Data not found in the other papers summarized herein.are presented below.

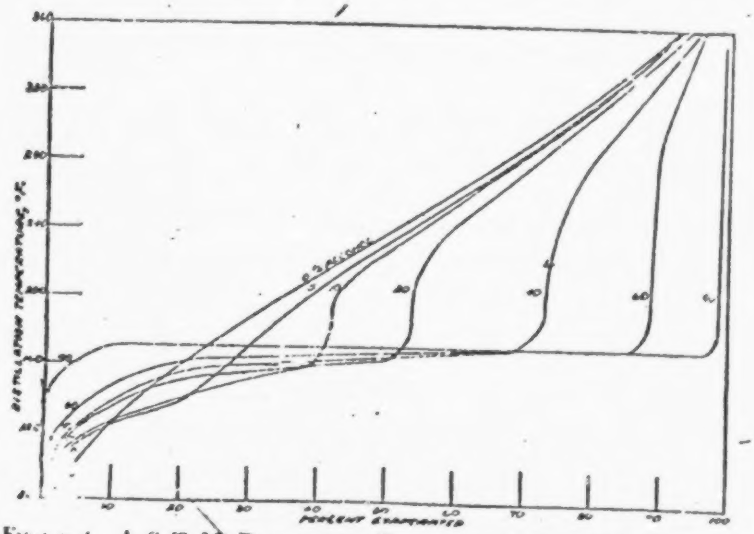
SPECIFIC GRAVITY of blends slightly lower then would be calculated from its components (See Table)

VISCOSITY of blends less then arithmetic average of components (See Table)

Blend % Ethanol	Sp.Gr.	Abs. Viscosity, poise
0	0.742	0.00525
10	0.746 (0.747)*	0.00552 (0.00646)*
100	0.794	0.01730

*Arithmetic Average

ASTM Distillation Curves



Fi... 4. A. S. T. M. Distillation Curves for Alcohol-Gasoline (10)

Water Tolerance

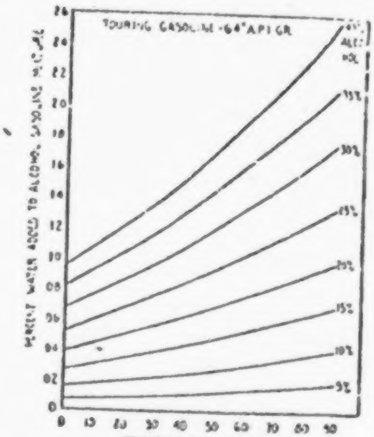


Figure 2. Percenta... Water That Can Be Added to Alc...ol-Gasoline Mixtures before Separation Occurs

RVP

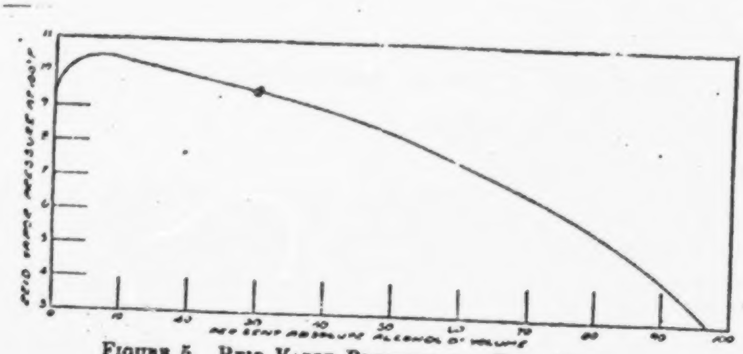


Figure 5. Reid Vapor Pressure for Fuel Mixtures

MON of low octane (61 MON) gasolines rate of increase approximately 9 units per 10%E.

BSFC The many data presented indicate the increased bsfc with a 10%E blend is approximately 4% based on both road and block tests.

EFFICIENCY rate of increase by using highest useable compression ratio is approximately 3% per 10%E. There is a corresponding decrease in bsfc of approximately 5% per 10%E.

COLD STARTING problems due to insufficient fuel vaporization will be greater for E blends. Attributed to higher latent heat vaporization and higher initial distillation temperature.

WARM STARTING problems due to high degree of fuel vaporization attributed to the increase in 100°F RVP for up to 30%E blends (see above).

CARBURETION for equal acceleration it was found that a carburetor setting giving 3% greater fuel flow was required. When carburetor was adjusted to give comparable mileage, acceleration and power was poorer.

VAPOR LOCK occurs when a portion of the fuel is vaporized. The following data shows the increased tendency of blends to form vapor which in turn causes vapor lock which is confirmed by experiments.

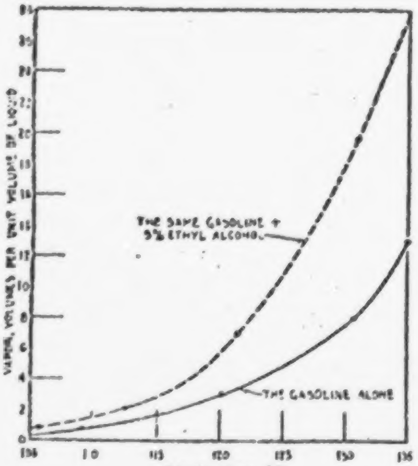


FIGURE 6. EFFECT OF ADDITION OF ETHYL ALCOHOL TO A GASOLINE UPON VOLUMES OF GAS EVOLVED AT VARIOUS TEMPERATURES

% E	Temp of Vapor Lock
0	118°F
1	113
2	110
3	110
4	111
5	111
10	112
20	114
30	116
40	118

LUBRICATION Combustion of alcohol increases tendency to burn lubricating oil from cylinder walls.

MATERIALS COMPATIBILITY

1) Solvent Properties - Problems reported with hoses, pump diaphrams, innercoatings of fuel tanks, lacquers (carburetor float shellac, paints).
2) Corrosion - water in blends causes corrosion. Sixty day immersion of a metal (unspecified) in gasoline with 20%E and 0.5%H_2O was 0.30 to 0.37 gm/m^2. Wear at low operating temperature for blend greater than gasoline:

Fuel	Cylinder wear	Top Piston Ring	(in/1000mi)
Gasoline	0.00044	0.0027	
83%E and 17%E	0.00080	0.0052	

At high operating temperature top piston ring wear was 0.00032 in/1000mi for both fuels, Valves reported to be more rapidly attacked by E blend.

Lichty, L.C. and Ziurys, E.J., (33).
ENGINE PERFORMANCE WITH GASOLINE AND ALCOHOL
Industrial and Engineering Chemistry, Vol. 28, No. 9, Sept. 1936

FUELS 1) 190 proof E neat
2) leaded (or Anilol) standard grade (Socony-Vacuum Company).

ENGINES CFR, 6 cylinder 1935 Chevrolet (5.45 CR)

TESTS Engine Dynamometer

PARAMETERS, MEASUREMENTS

CFR	T_{wi} = 212°F	ihp
	T_{oil} = 212°F	isfc
	T_{mix} variable	T_{exh}
	ϕ variable	η_v
	SA variable	

6 cyl	T_{air} = 100°F	ihp
	ϕ variable	isfc
	SA variable	intake port temperature
	RPM variable	

THEORETICAL CONSIDERATIONS

CHARGE HEATING VALUE: @ϕ =1, & dry charge E has 0.6% less heating value.

MIXTURE VAPORIZATION: Air Vapor ratios calculated; ethanol 54% evaporated if same heat as 100% gasoline vaporization.

SPECIFIC HEATS: E 7.42, G 7.26 (avg. 1000-4000°F) indicating 2.2% lower T & P rise for ethanol.

MOLAR EXPANSION: E has 0.8% advantage (6.52% increase ethanol, 5.76% increase octane).

WATER in 190 proof ethanol: displaces 1.1% mixture @ 100% evaporation; reduces heating value per gal. 6.2%.

TEST RESULTS - CFR

MIXTURE TEMPERATURE: E 35°F lower @ϕ =1 with no mixture heating.

EQUIVALENCE RATIO for Maximum Power: E 1.21; G 1.26.

MIXTURE TEMPERATURE: E 30°F lower @ maximum power ϕ with no mixture heating.

VOLUMETRIC EFFICIENCY at max power ϕ:E is 5% greater with no mixture heating; E is 7% greater with mixture heating.

SPARK ADVANCE for Best Power: E about 2° more SA than gasoline.

MAXIMUM POWER: E 1.5% greater with unheated mixture; E 3.2% greater with heated mixture.

ISFC: not appreciably affected by mixture heating.

ISFC: 70% higher @ϕ =1.

ISFC: 60% higher @ maximum power ϕ .

ISFC: higher even using higher allowable CR.

EXHAUST GAS TEMPERATURE: not appreciably affected by mixture heating, slightly lower for E.

TEST RESULTS 6 Cylinder

MAXIMUM IHP @ WOT: about same (3% more @ 2000RPM, 3% less @ 3000 RPM).
MAXIMUM IHP @ 2/3 LOAD: 3% lower @ 1000RPM, 5% higher @ 2000RPM.
MAXIMUM IHP @ 1/3 LOAD: about same @ 1000RPM, 5% higher @ 1500RPM.
MAXIMUM IHP : average gain of 2% is about same as experimental error.
ISFC : independent of load @ RPM >1000 for ethanol (>1500 for gasoline).
ISFC at max power ϕ } 63% higher @ 1000RPM, 58% higher @ 3000RPM.
ISFC for multicylinder } greater than for CFR engine. Ethanol 14.7% greater; gaso
11.3% greater (due to combustion chamber; distribution

Lichty, L.C. and Phelps, C.W. (Yale University), (36).
CARBON MONOXIDE IN ENGINE EXHAUST USING ALCOHOL BLENDS
Industrial and Engineering Chemistry Vol.29, No.5, May 1937

FUELS 1) Standard grade nonleaded gasoline (Super Shell): I.P.-90°F; 50% point 227°F; 90% point 398°F, SG= 0.738 @ 60°F
2) Anhydrous denatured ethanol
3) 10% and 20% ethanol blends of above
4) Pure absolute ethanol

ENGINES CFR, 1935 Chevrolet 6 cylinder

TESTS Engine Dynamometer

PARAMETERS, MEASUREMENTS

CR	N
ϕ	Torque
CO	Manifold heat to CFR

RESULTS (CFR Engine)
[AF @ ϕ =1: 15.1 (C_8H_{18}); 14.4 (10%E); 13.8 (20%E)from chemical balance.]
CO @ ϕ =1: 0.1%(gasoline); 0.1%(10%E); 0.3%(20%E)
CO for pure ethanol same as denatured ethanol
Maximum IHP: 4.67(gasoline); 4.61 (10%E); 4.56 (20%E)
Maximum IHP ratio: 1 (gasoline); 0.99 (10%E); 0.98 (20%E); $\phi \approx 1.1$ ea.fuel
Blend Leaning Effect - increase in AF:1-2%(10%E); 2-3% (20%E).

RESULTS (6 cylinder)
Distribution, as determined from exhaust part CO measurements is not appreciably influenced by the nature of the fuel, (gasoline, 10%E, 20%E), but is more dependent upon speed, throttle position, design of carburetor, manifold, etc.

Lichty, L.C. and Phelps, C.W. (Yale University), (42).
GASOLINE-ALCOHOL BLENDS IN INTERNAL COMBUSTION ENGINES
Industrial and Engineering Chemistry, Vol. 30, No.2, January, 1938

FUELS
1) Commercial non-leaded gasoline, 67ON (tel added in some tests)
2) Third-grade gasoline, 58ON
3) Secondary reference fuel C-10, 78ON
4) 5, 10 and 20% blends of anhydrous ethanol with the above

ENGINES CFR, 1935 6 cyl. Chevrolet engine with heated inlet air

TESTS Engine Dynamometer

PARAMETERS, MEASUREMENTS

CFR

MON	$T_{exhaust}$
CR = 5,6.2, 6.8	ϕ variable
N = 1200 RPM	η_v
Optimum Spark	ihp,bhp
T_{inlet}	bsfc
Inlet Heated	$T_{exhaust}$

6 cyl.

N = 1,2 & 3000RPM	
T_{inlet} = 100°F	
η_v	mep
ihp	bhp
ϕ	η_b
bsfc	

RESULTS - CFR ENGINE

OCTANE NUMBER - Motor Method. Data shows: less MON increase in bare fuels having higher MON; rate of increase with ethanol addition decreases as % ethanol in blend increases

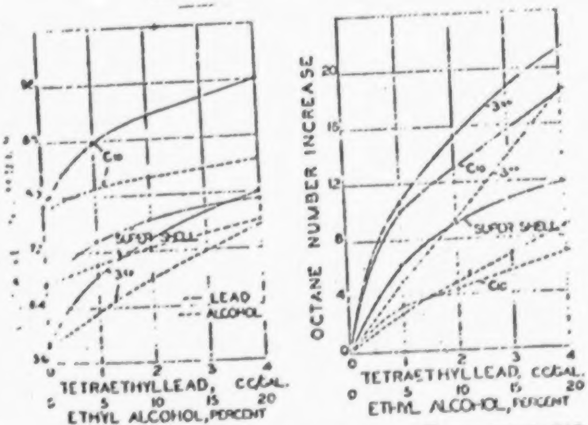


Figure 1. Effect of Ethyl Alcohol and Tetraethyllead on Octane Number

MIXTURE TEMPERATURE in the intake manifold found to decrease as compared to gasoline. The decrease was 4°F for 10%E and 8°F for 20%E. This compares with 11°F for 10%E measured by Brown and Christensen

VOLUMETRIC EFFICIENCY data does not show a consistent increase with the blends.

IHP, BHP - @ same ϕ essentially the same for blends and gasoline; max power ϕ =1.08, gasoline; 1.07, 10% blend; 1.09, 20% blend.

INLET MIXTURE HEATING reduced power output. Reduction was ≈5% @ manifold heat ≈4% of ihp, and ≈ 10% @ manifold heat ≈9% of ihp.

BSFC @ ϕ = 1 increased on the average 5.7% for 10%E and 12% for 20%E.

EFFICIENCY @ ϕ=1, based on linear mixing lower heating value, increased on the average 3% for 10%E and 9% for 20%E.

EXHAUST TEMPERATURES reach a maximum value for each fuel near $\Phi = 1$.

RESULTS 6 cylinder engine

VOLUMETRIC EFFICIENCY measurements vary less than 2% for the various fuels and do not show any consistant trends.

IHP @ part load essentially the same for gasoline and blends at same Φ

BSFC average increased: 5%, 10%E; 9%, 20%E. @ both maximum power and maximum economy air-fuel ratios.

BRAKE THERMAL EFFICIENCY for the blends at comparable conditions is essentially the same as for gasoline.

COOLING WATER HEAT REJECTION practically the same for blends and gasoline.

Rogowski, A.R. and Taylor, C.F. (M.I.T.) , (49).
COMPARATIVE PERFORMANCE OF ALCOHOL-GASOLINE BLENDS IN A GASOLINE ENGINE
Journal of Aeronautical Sciences, V.8, 1941

FUELS 1) 70 ON Regular grade gasoline
2) Blends of above and 10, 25 and 50%(vol.) anhydrous ethyl alcohol; A.S.T.M. distillation curves presented
3) 95% ethyl alcohol neat

ENGINES CFR, 1938 Buik 8, 1934 Chevrolet 6
TESTS Engine Dynamometer
PARAMETERS, MEASUREMENTS

$T_{air\ inlet}$	bsfc	throttle setting
CR	N	
bmep	Φ	

TEST RESULTS
OPTIMUM (minimum sfc @ best power Φ)
INLET TEMPERATURE Provided the inlet temperature was at least 100°F for gasoline the other blends should be: 10%E and 25%E same as gasoline; 50%E, 30°F higher; neat E, 140°F higher.

WOT POWER Blends up to 25%E @ optimum CR yield 10 to 12% more power than 70 ON gasoline with no increase in BSFC. Above 50% blend BSFC increases.

COMPUTATIONS Based on the test results, calculations were performed which predict the following changes when 10 or 25%(vol.)E is added to 70 ON gasoline.
1) For the same CR and carburetion but optimum spark:
   a) increased WOT power, if CR >5.5; b) increased part throttle bsfc.
2) For same CR but optimum carburetion and spark:
   a) increased WOT power; b) increased part throttle bsfc.
3) For optimum CR, carburetion and spark:
   a) increased WOT power, b) slight increase in bsfc
4) For engines redesigned to give same WOT bhp, 10% and 25%(Vol.)E gives slightly lower bsfc.

Brooks, D.B., (52).
SINGLE-CYLINDER ENGINE TESTS OF SUBSTITUTE MOTOR FUELS
National Bureau of Standards Research Paper RP1660
Journal of National Bureau of Standards, Vol.35, July 1945.

FUELS
1) Two Reference gasolines, MON = 70 RON = 72
2) 190 Proof Ethanol
3) 200 Proof Ethanol

Other fuels tested are not considered in detail

ENGINE CFR with intake manifold injection

PARAMETERS, MEASUREMENTS

CR = 5.11 and CR for trace knock @ best power ϕ and optimum SA	
SA variable	Combustion chamber wall temperature
ihp	
isfc	

RESULTS

@ CR = 5.11 values except for SA (deg BTDC) are ratios = value for fuel ÷ value for gasoline A (G_A)

FUEL	ihp	min.bsfc.	max η_b	Optimum SA
G_A	I	I	I	47.5
190pE	1.052	1.65	1.04	47.0
200pE	1.045	1.54	1.03	46.9
G_B^*	1.000	1.01	0.99	45.0

CR for trace knock was 5.11 for gasolines and 9.91 for the Ethanols.

IHP was found to be directly related to fuel heat input for the various fuels tested.

OPTIMUM SA found to be essentiably the same for various fuel heat input rates (BTU/lb air) except gasoline which required somewhat greater SA at lean mixture.

COMBUSTION CHAMBER WALL TEMPERATURE was measured by a thermal plug screwed into the cylinder head. At trace knock gasoline was ≈ 10°F higher than ethanol, except at lean mixtures where ethanol temperature was greater. At equal CR = 5.11 gasoline temperature ≈ 50°F to 70°F higher than ethanol.

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* Gasoline B

Duck, J.T. and Bruce, C.S., (53).
UTILIZATION OF NONPETROLEUM FUELS IN AUTOMOTIVE ENGINES
National Bureau of Standards Research Paper RP1681
Journal of Research of the NBS, Vol. 35, December, 1945

FUELS 1) G-Regular 72ON
2) 190 proof E neat
3) 200 proof E neat
lower proof E tested but not included here

ENGINES Two 1942 Plymouth, one 1942 Chevrolet, one 1940 Ford V-8

TEST Engine Dynamometer

PARAMETERS, MEASUREMENTS

SA variable	bhp	Distribution by spark plug electrode temperature
N 1500 RPM	bsfc	
Φ variable	η_b	Air Flow CO_2 P_{man}

TEST RESULTS

	WOT bhp (Ratio)				Maximum η_b, % (Ratio)			
FUEL	Plym	Chev	Ford	Plym 4	Plym	Chev	Ford	Plym 4
G	47.8 (1.000)	46.5 (1.000)	43.7 (1.000)	45.8 (1.000)	24.0 (1.000)	24.6 (1.000)	23.5 (1.000)	25.3 (1.000)
190 E	49.0 (1.025)	46.8 (1.006)	44.0 (1.006)	47.2 (1.031)	29.4* --	25.4 (1.033)	23.7 (1.009)	26.1 (1.032)
200 E	50.5 (1.056)	47.8 (1.028)	44.2 (1.011)	47.6 (1.039)	27.6* --	24.7 (1.004)	23.5 *1.000)	26.0 (1.028)

*Values Suspected of being too large. Essentially the same for the 3 fuels listed (between 16.5 and 19° BTC).

MAX. POWER SPARK : The lower proof alcohols required greater advance

Best efficiency Φ at road load	mph	20	30	40	50
	200E	0.86	0.80	0.75	0.81
	G	0.90	0.91	0.83	0.84

MAXIMUM CO_2 found near $\Phi = 1$, G had lower CO_2 than E.

DISTRIBUTION with Plym 4: E good @ 50mph, very poor @ 20mph; G good @ 50 and 20 mph.

MALDISTRIBUTION with E found to vary from engine to engine.

MANIFOLD TEMPERATURE INCREASE lowered power output; improved distribution.

MALDISTRIBUTION affected fuel consumption more than power output

CARBURETORS require relesign of all basic parts for satisfactory use with E.

FUEL CONSUMPTION found to be inversely proportional to its heat of combustion.

Pleeth, S.J.W. , (67).
ALCOHOL MOTOR FUELS
Automobile Engineer, April, 1952

This is a survey paper as outlined below:

POWER OUTPUT, FUEL CONSUMPTION AND HEATING VALUE

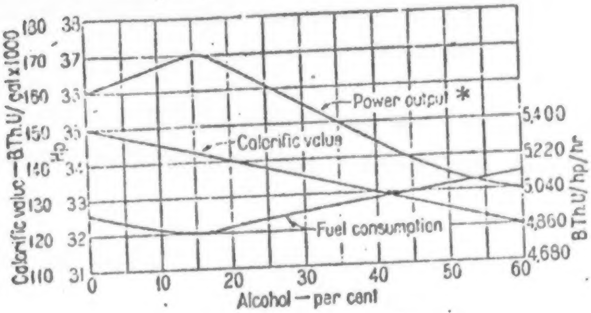

Fig. 1. Influence of alcohol content

OCTANE RATINGS

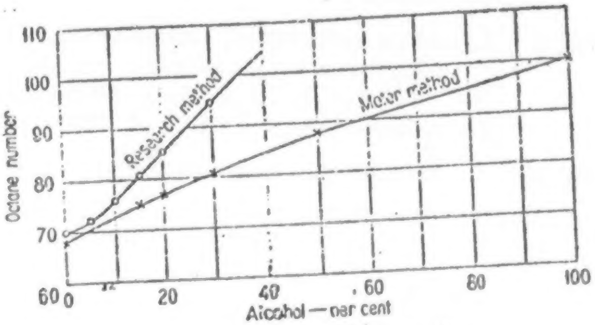

Fig. 2. Determination of octane numbers

Pleeth points out that the decrease in octane member during sudden throttle opening due to the lag of tel containing liquid gasoline droplets will not be observed in an ethanol blend. Rather, the readily vaporized ethanol/HC azeotrope will result in a higher antiknock fuel being delivered to the cylinders on sudden throttle opening.

RVP and VAPOR LOCK - RVP test procedure applied to a blend results in separation of ethanol from gasoline due to water in the test sample. The measured RVP is thus lower than the actual vapor pressure of the blend. When such a blend is compared with a gasoline of RVP equal to the erroneous, measured value the blend will exhibit a tendency to vapor lock. If a blend is compared with a gasoline both having the same vapor pressure no difference in vapor locking tendency can be found.

WARMING UP PERIOD - In winter power output from a cold engine is reduced but,with normal induction heating, the effect is slight and of short duration.

Refers to Swedish Government study (circa 1927-37): found public to be unaware that the alcohol blend is different than gasoline.

WATER ABSORPTION - Refers to tests with 10%E blend with relatively large samples (500ml, 5,500gal. and 84,000 gal.), open to the atmosphere, where the cloud point remained essentially constant (-60 to -58°C). A small sample however (50ml) showed considerable increase within 15 days indicating water absorption. Indicates that off-vehicle storage of ethanol blends not a problem. On vehicle blend water tolerance problems, if any, will be encountered during initial use of blend, thereafter there should be no problem. Separated blends are fatal during startup but tolerable if the engine is warm.

* Compression ratios not constant

Porter, J.C. and Wiebe, R. (Northern Regional Res.Lab.,Peoria, Ill.) , (69)
ALCOHOL AS AN ANTIKNOCK AGENT IN AUTOMOTIVE ENGINES
Industrial and Engineering Chemistry Vol.44, No.5, May, 1952.

THEORETICAL CONSIDERATIONS - Otto cycle calculations show approximately 1% higher thermal efficiency and 40°F lower peak temperature for a 25% ethanol blend compared to gasoline for a range of compression ratios from 6 to 12. Calculations assumed fuel to be initially 100% vapor.

FUELS 1) Straight-run, catalytically cracked, thermally cracked and polymer base stock gasolines. Also shale gasoline with various (0.13, 0.22 and 0.3%(wt)) sulfur content.
2) Above with 10% and 25% ethanol.

ENGINES Knock rating engine; Ford 6 cyl, 6.8CR and GM, 10 CR

MEASUREMENTS RON, MON, ROAD ON (Modified Uniontown and Borderline Method @ 1000, 1500, 2000, 2500 and 3000RPM

TEST RESULTS
BORDERLINE ON = RON @ 1000RPM for gasolines for both 6.8 and 10 CR
BORDERLINE ON = MON @ 2500RPM for gasolines @ 6.8 CR
BORDERLINE ON > MON @ 2500RPM for gasolines @ 10 CR
BORDERLINE ON = RON @ 1000RPM for 10% blend @ 6.8 and 10 CR
BORDERLINE ON > RON @ 1000RPM for 25% blend @ 6.8 and 10 CR
BORDERLINE ON = MON @ 2500RPM for 10% and 25% blends @ 6.8 CR
BORDERLINE ON > MON @ 2500RPM for 10% and 25% blends @ 10 CR

(RON characteristic of low speed 1952 vehicle operation and MON of high speed vehicle operation).

In previous work (the authors report) it was shown that methanol is for all practical purposes equivalent to ethanol in antidetonant mixtures.

SHALE OIL GASOLINE sulfur content (0.13, 0.22, 0.36%) found not to affect octane increase with ethanol addition.

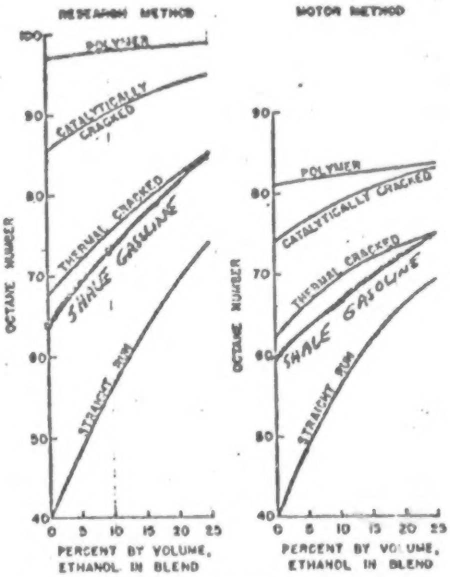

Figure 4. Variation of Octane Rating with Per Cent of Ethyl Alcohol in Fuel-Alcohol Blends

Southwest Research Institute, (76).
PERFORMANCE OF COMMERCIAL GASOLINES BLENDED WITH 5%, 10% and 25% ETHANOL
December, 1956

FUELS 5,10 and 25% (Vol) Anhydrous Ethanol in 3 regular (90-91RON, 81-83MON) and 3 premium (98-100RON, 89-91MON) gasolines

ENGINES Single cyl (knock rating) and 1955 Chrysler 331 cu in V-8.

TESTS MON, RON, Borderline Road Rating ON, Distillation Curves, Water Tolerance

TEST RESULTS

RON - Increased for the regular and premium gasolines. Increase less for the premiums.

MON - Increased for the regular gasoline. Decreased for the premiums.

ROAD ON - Increased slightly for regulars. Decreased at 3000RPM, remained same at 1600-2000RPM for the premiums.

RVP - Slight decrease

20% EVAPORATION POINT lowered; may help @ moderately low starting temperatures.

INITIAL B.P. raised so extreme low temperature starting would probably not be improved.

WATER TOLERANCE - % by volume to cause turbidity at 38°F: @ 5%E, $\approx$0.08% H_2O; @ 10%E$\approx$0.35% H_2O; @ 25%E,$\approx$1.35% H_2O

DISTILLATION CURVES exhibit 50% point depression of 36 to 74°F.

Bolt, J.A. (University of Michigan) , (94).
A SURVEY OF ALCOHOL AS A MOTOR FUEL
SAE SP-254, June, 1964

This is an excellent survey including an extensive bibliography. Portions of the summary are quoted below.

POWER Ethyl alcohol as a fuel makes possible up to about 8% more power output, the increase varying down to zero, depending on the amount of heat added to the engine induction system.

OCTANE The value of ethyl alcohol as an octane improver has been greatly reduced, and may be expected to diminish further if the octane number of gasoline continues to increase.

AIR FUEL RATIO A 25% ethyl alcohol blend substituted for gasoline without carburetor changes, results in a mixture about 10% leaner on the basis of Btu/lb of air; in other words, there will be 10% more air available for the combustion of the alcohol.

EXHAUST EMISSIONS Since exhaust emissions are very dependent on the quantity of air available for combustion, it is most important that comparative tests of emissions be conducted on the basis of an equivalent amount of air for each. This requires different carburetor settings for alcohol and gasoline.

No published evidence has been found to indicate that the use of ethyl alcohol as a constituent of motor fuel will help appreciably in solving the air pollution problem.

WATER TOLERANCE Because of the low water tolerance of alcohol-gasoline blends, anhydrous ethanol must be used and great care must be exercised to avoid water contamination. For the 25% alcohol blend, less than 2% of water will cause separation.

Gross, G.P. (Esso Research) , (95).
DISCUSSION SECTION OF SAE SP-254, June, 1964

FUELS 1) Isooctane
2) A premium gasoline
3) Blends of above and 25%(V) Ethanol

ENGINE CFR with RDH hemispherical cylinder head and fuel injection into intake manifold.

PARAMETERS, MEASUREMENTS

Iso & E/I Blend	Gas & E/G Blend	SA=35°BTC	HC-FID & NDIR
N = 1500RPM	N = 2000RPM	ϕ variable	NO-Phenol-disulfonic acid method
P_{man} = 15 inHg	P_{man}=15.9 inHg	CO_2	
		CO_2	O_2

TEST RESULTS

CO_2, CO, O_2 and NO Emission concentrations the same for both both Iso / E blend and plain Isooctane when compared at same oxygen as % of stoichiometric.

HC emission concentration*- same results as above when FID and NDIR used but NDIR values lower.

NDIR HC concentration* for gasoline and E and gasoline same but lower than NDIR HC measured for Isooctane.

*Exhaust sample cooled by ice water and filtered; NDIR Hexane sensitized.

Jackson, M.W., (100).
EXHAUST HYDROCARBON AND NITROGEN OXIDE CONCENTRATIONS WITH AN ETHY ALCOHOL-GASOLINE FUEL
SAE SP-254, June, 1964

FUELS 1) Leaded 99RON, 90MON, 66% Saturates, 7% Oletins, 27% Aromatics summer grade gasolines
2) 75%(wt) blend of above gasoline and 25%(wt) anhydrous ethanol denatured with 9.1%(wt) methanol.

ENGINE Single cylinder, 8.9 CR with fuel injected during early intake stroke.

TESTS Engine Dynamometer (simulating 15-30mph acceleration) and various vehicles.

PARAMETERS, MEASUREMENTS

N = 1200RPM	Torque
SA = mbt	HC (NDIR & FID)
Φ variable	NO modified phenol disulfonic acid method

TEST RESULTS

HYDROCARBONS 1) FID HC concentrations ≈1.5-2.0 times higher than NDIR. 2)@ same Φ NDIR HC concentration essentially the same for both fuels. 3)@ same Φ FID HC concentration lower for blend but attributed to lower FID response to ethanol.

NITROGEN OXIDE:@ same Φ addition of ethyl alcohol results in slightly higher nitric oxide concentration : 6% @ Φ =1.1; 10% @Φ=1 and Φ = 0.9.

PERFORMANCE: to achieve same vehicle performance with blend Φ must be about the same as that used with gasoline.

TORQUE: @ the same Φ, torque for the blend is essentially the same as for gasoline.

AIR FUEL RATIO: for two 1963 and one 1964 model cars was found to increase by only 0.2 ratios with the 25% blend.

SURGE: was found to be more severe with the blend. One 1963 vehicle became commercially unacceptable.

WARMING: problems encountered with blend in two 1964 models. With another 1964 model none were encountered.

CARBURETION: changes appear necessary if ethanol is added to gasoline in appreciable amounts on any widespread basis.

Lawrason, G.C., and Finigan, P.F., (101).
ETHYL ALCOHOL AND GASOLINE AS A MODERN MOTOR FUEL
SAE SP-254, June, 1964

FUELS
1) 100 RON gasoline with phosphorous antifouling agent
2) 98 RON blend of 92.5 RON, unleaded, catalytically cracked gasoline and 3.0 ml of tel/gal.
3) 97.5 RON blend by volume of 75% 92.5 RON unleaded catalytically cracked gasolene and 25% 200 proof ethanol.
4) 92.5 RON, unleaded, catalytically cracked gasoline plus 25% by volume 190 proof denatured ethanol.

ENGINES
1962, Oldsmobile V-8, CR = 10.25
1952, Chevrolet 6, CR = 6.6
GM ES-59, V-8, CR = 12

TESTS Engine Dynamometer
PARAMETERS, MEASUREMENTS

RPM - variable	bsfc	mpg	Oil neutralization number
Throttle - variable	bhp	deposits	Oil sulfated Ash
SA - standard & optimum		wear	Oil viscosity (100 & 210°F)

HC	- Infrared Spectrophotometer
NO_2	- Modified Phenol Dilsulfonic Acid Method

TEST RESULTS

HYDROCARBONS 10 to 30% reduction with ethanol blend (fuel 3) compared to gasoline (fuel 2). [Reduction, however, is attributed to the lean mixtures delivered by the standard carburetor with the ethanol blend].

ETHANOL: Unburned ethanol failed to show in exhaust

OXIDES OF NITROGEN (ppm) ethanol blend 3 ÷ (ppm) gasoline @ road load		52 Chevy	62 Olds	GMES-59
	Idle	1.32	1.00	1.00
	1000 RPM	1.06	1.55	0.73
	2000 RPM	0.11	1.08	1.03
	3000 RPM	0.48	0.97	0.96

DEPOSITS Unleaded, ethanol blend 3 produced about one-fifth deposit weight of tel blend 2 and one-seventh that of commercial gasolene blend 1. Deposits from tel blend were, however, 85% lead compounds.

WEAR After 200 hours the wear with ethanol blend 3 and tel blend 2 was essentially the same.

OIL NEUTRALIZATION NUMBER & SULFATED ASH Ethanol blend 3 showed significantly less change in both of these parameters.

VISCOSITY @ 100°F For fuels 1 and 2 viscosity still less than original value after 200 hour operation while with ethanol blend viscosity increased about 0.4%.

VISCOSITY @ 210°F At 200 hour operation with tel blend 2 and with ethanol blend 3 engine tube oils had essentially the same viscosity; about 1% higher than original value. Fuel 1 viscosity was still lowe than original after 200 hours.

BSFC @ WOT fuels 2 and 3 essentiall the same bsfc (62 Olds)

BSFC @ 1/4, 1/2 and 3/4 throttle ethanol blend 3 bsfc approximately 12% higher than tel blend 2 (62 Olds).

MAX POWER Essentially the same with standard ignition and carburetion for ethanol blend 3 and tel blend 2. Slight (5bhp) increase if timing is optimized for ethanol blend (1962 Olds).

BSFC VERSUS HOURS OF OPERATION Up to about 150 hours the ethanol blend 3 exhibited higher bsfc than that of the commercial gasoline blend 1. BSFC of blend 1 started to increase however, and became equal to that of the ethanol blend at 200 hours.

MPG Commercial gasoline and 200 proof ethanol blend 3 exhibited essentially same mpg up to 70mph then ethanol blend mpg became lower. The 190 proof blend exhibited lower mpg up to 70mph then for higher speeds equaled that of the 200 proof blend.

Extra heating of intake manifold (couple of degrees temp. rise) had no measurable effect on bsfc for ethanol blend.

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Starkman, E.S., Newhall, H.K. and Sutton, R.D., (103).
COMPARATIVE PERFORMANCE OF ALCOHOL AND HYDROCARBON FUEL
SAE SP-254, June, 1964

FUELS
1) Isooctane
2) Ethanol
3) Methanol

ENGINE CFR with fuel injection intake manifold just ahead of intake valve

PARAMETERS, MEASUREMENTS

N = 1800 RPM	CR = 9
$T_{air} = 100^oF$	Φ variable
P_{air} = 14.7 psi	isfc

THEORETICAL CONSIDERATIONS

Thermodynamic equilibrium property charts are presented for methanol, ethanol and benzene burned mixtures. These charts are used to perform idealized cycle calculations (isentropic compression and expansion, constant volume combustion). Consideration is also given to the effect of fuel vaporization during compression. Dry refers to 100% fuel vapor at beginning of compression, wet 0%.

Molar Expansion Ratio Gain Over Isooctane:

	No Dissociation	With Dissociation
Dry	M-4% E-0.8%	M-1% E-2%
Wet	M-12.6% M-6.1%	M-13% E-7%

ENERGY IN CHARGE BTU/lb air for stoichiometric mixture advantage over isooctane:M 6.7%; E 1.6%.

IDEALIZED CYCLE CR = 9; Φ = 1; Intake air 14.7 psi, 100^oF:

	Compression Work Ratio*		Peak Temp ^oR		imep Ratio*	
	Dry	Wet	Dry	Wet	Dry	Wet
C_8H_{18}	1.00	0.97	5220	5200	1.000	1.01
E	1.07	0.83	5135	5000	0.946	1.00
M	1.19	0.75	5100	4870	0.927	1.094

*Ratios are: Value for fuel / Value for C_8H_{18} Dry
imep ratio almost independent of compressio ratio

TEST RESULTS

imep*(ratio)	@ Φ = 1	maximum	@minimum isfc
C_8H_{18}	154(1.00)	159(1.00)	148 (1.00)
E	148(0.96)	166(1.04)	135 (0.91)
M	161(1.05)	174(1.09)	148 (1.00)

Φ @ minimum isfc
0.9
0.9
0.82

*psi

MAX IMEP can be increased by about 6% with ethanol as compared to isooctane;about twice the fuel flow rate is necessary

MAX IMEP can be increased by about 12% with methanol with about three times the fuel flow rate of isooctane

BEST ECONOMY EFFICIENCY RATIO (Alcohol/Isooctane): E 0.87; M 1.0

Taliaferro, H.R., (104).
DISCUSSION SECTION OF SAE SP-254, June, 1964
(The following is quoted from SP-254)

VAPOR LOCK "The results of RVP and ASTM distillation tests on a typical Chicago summer season gasoline, and a blend of this gasoline with 25%(v) of 200° proof ethanol, are presented. The blend was 0.4 pounds higher in RVP and the temperatures for 20,30, and 50 percent evaporated were markedly lower than for the gasoline. We compared the relative vapor-locking tendencies of the gasoline and the blend by determining the temperatures for several levels of vapor to liquid ratio in the Union Oil apparatus. At vapor to liquid ratios of 20 or 30 to 1, ratios at which car-fuel systems encounter vapor lock, the temperatures for the blend are four to five degrees lower than those for the gasoline indicating the blend would encounter incipient vapor lock at four to five degrees lower ambient temperature than the gasoline. Low-cost butane, and other light hydrocarbons, would have to be withdrawn from the ethanol-gasoline blend to provide vapor-lock protection equivalent to that provided by the gasoline."

Ninomiya, J.S., Golovog, A., Labana, S.S. (Ford Motor Company), (119).
EFFECT OF METHANOL ON EXHAUST COMPOSITION OF A FUEL CONTAINING TOLUENE, N-HEPTANE, AND ISOOCTANE
Journal of Air Pollution Control, Assoc. Vol.20, No.5, May, 1970

FUELS Up to 25% Methanol in a blend of toluene, isooctane and N-heptane. RON maintained @ 93.

ENGINE Labeco CLR single cylinder, CR = 7.6

TESTS Engine dynamometer

PARAMETERS, MEASUREMENTS

N = 1500 RPM	Methanol concentration 0 to 25%
Torque = 21 ft.lb.	$0.8 < \phi < 1.2$; $[1.25 > (1/\phi) > 0.83]$
SA @ MBT	ϕ Based on CO, CO_2 and O_2 measurements
$T_{coolant}$ = 190°F	Aldehydes - MBTH
T_{oil} = 170°F	HC - Gas Chromatograph
T_{exh} = 1.7 inHg	CO, CO_2, NO - Infrared Spectrophotometer

TEST RESULTS Exhaust Gas Temperature of 1180°F not affected by methanol addition.

CO_2 CO, NO, O_2 Concentration not altered by addition of up to 25% Methanol when compared at same ϕ

HC - the effect of Methanol on HC subsides as mixture is made lean until @ $\phi = 0.8$ there is no effect.

FORMALDEHYDE & HC EMISSIONS

Data presented as ppm or per lb. of fuel constituent identified as being the source of the exhaust constituent.

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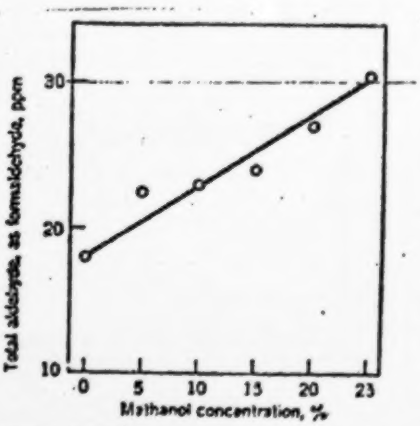

Figure 2. Relation between total exhaust aldehyde and methanol content in fuel; 0.85 equivalence ratio. *

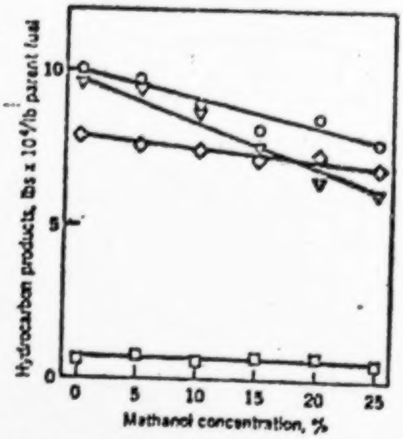

Figure 3. Exhaust hydrocarbons vs methanol content in fuel, at 0.85 equivalence ratio: (○) methane; (▽) isobutylene; (◇) propylene; (□) acetylene.

*Equivalence ratio used in (119) is the Air-Fuel equivalence ratio 1/ϕ. Thus 0.95 equivalence ratio is

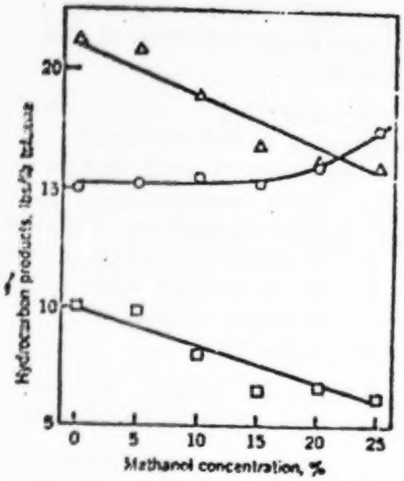

Figure 4. Exhaust hydrocarbons vs methanol content in fuel, at 0.85 equivalence ratio: (△) ethylbenzene × 10^4; (○) benzene × 10^4; (□) styrene × 10^5.

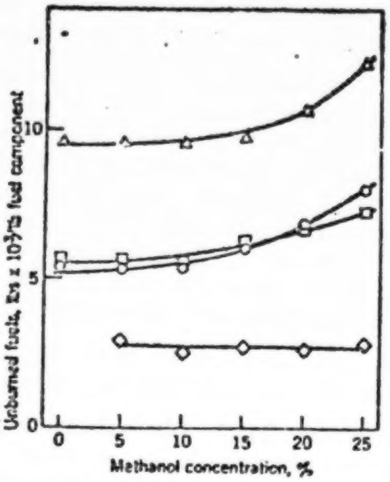

Figure 5. Unburned fuel components in exhaust vs methanol content in fuel, at 0.85 equivalence ratio: (▽) toluene; (○) isooctane; (□) n-heptane; (◇) methanol.

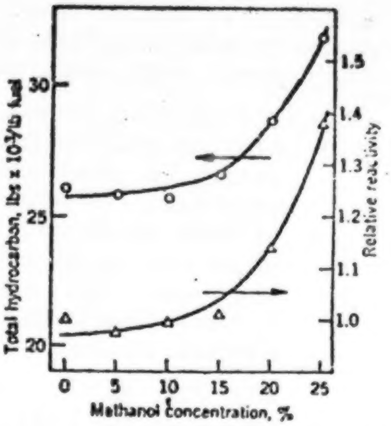

Figure 6. Total exhaust hydrocarbon (○) and relative reactivity (△) vs methanol content in fuel, at 0.85 equivalence ratio.

THEORETICAL CONSIDERATIONS Discussions are presented describing the mechanisms by which the various exhaust constituents are formed and react.

CONCLUSIONS (quoted from paper)

1. "Under fuel-rich conditions, additional formaldehyde-derived from methanol-inhibits decomposition of parent fuel molecules, thus increasing unburned fuel in the exhaust."
2. "The increase in formaldehyde concentration with increasing methanol content in the fuel results in less olefins and substituted benzenes in the exhaust. These observations are explained by the reactions of formaldehyde with alkyl radicals."
3. "The photochemical reactivity of the exhaust, under fuel-rich conditions, increases with rise in methanol content because unburned toluene in the exhaust rises with addition of methanol."
4. "Methanol-hydrocarbon blends do not reduce exhaust hydrocarbons when the engine is operated at a performance level comparable to the methanol-free blend."

Keller, J.G., Douthit, W.H., Long, W.C. and Taliaferro, H.R. , (122).
USE OF ALCOHOL IN MOTOR GASOLINE - A REVIEW
The Committee for Air and Water Conservation
American Petroleum Institute, Publication No.4082, Aug. 1971

This report treats the available data in 1971 on the use of ETHANOL in motor fuel with some attention given to METHANOL. Their summary and conclusions are listed below as well as some of the data, they presented,some of which was not found elsewhere.

OCTANE "Ethyl alcohol by itself has good antiknock quality. It shows high blending octane values in low octane unleaded fuels when rated in the single cylinder laboratory ASTM Research and Motor engines. However, with unleaded fuels, there is a depreciating effect on Motor octane number and thus these high blending values have not been observed with alcohol blends in modern multicylinder engines. The addition of ethyl alcohol will not provide the same octane improvement that can be obtained more economically from either refinery processing of the use of lead alkyls."

ETHANOL NEAT: RON 106 to107.5; Mon 89 to 90 and METHANOL NEAT: RON 106 to 115; MON 88 to 92 (value depending on source of data).

PERFORMANCE AND FUEL CONSUMPTION No advantage in vehicle performance can be found by using alcohol as a fuel supplement or component. On the contrary, use of an alcohol-gasoline blend can result in a serious loss of driveability. Problems with alcohol-gasoline blends on current emission control vehicles would consist of "tip-in" or acceleration hesitation, poor throttle response during warm-ups, and loss of mileage. Certain alcohol-gasoline blends may provide equivalent power output with a small loss in fuel economy* (compared to commercial gasoline); but in lower compression engines, fuel economy suffers significantly. Data below is from Esso Research and Engineering Co. 1949:

	Relative mpg		No Carburetor Adjustment**		Carb.Adj.for Max.Power	
FUEL	Road	Lab.	Power Incr.+	Fuel Cons.++Incr.	Power Incr.	Fuel Cons. Incr.
100%G	100	100	-	-	-	
10%E	98.3	98.5	3.4%	1.3%	3.8%	5.2%
20%E	96.0	96.3	-	-	-	
25%E	-	-	4.7%	4.8%	6.7%	0.1%
30%E	93.3	93.8	-	-	-	-
100%E	68.0	58.0	-	-	-	-

A 1970 Union Oil Co. memorandum referred to states that "with normal carburetor settings a 10% methanol blend could be used with satisfaction and that fuel consumptions remains almost exactly the same as with the gasoline alone".

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*mpg
** Average data for 5.5, 6.5 and 7.5 CR; SA adjusted for each fuel.
+ Incr.= Increase
++ Cons.= Consumption

In a 10.25 CR 1962 Oldmobile V8 a 25%E blend in 92.5RON gasoline little difference was observed in max bhp with standard carburetor and SA. Volumetric fuel consumption was equal to gasoline in many instances.

Authors point out that optimum alcohol blending for power and economy is dependent on the characteristics of the engine.

EMISSIONS At an equivalent Φ, alcohol-gasoline blends give the same levels of carbon monoxide, hydrocarbons and oxides of nitrogen as conventional gasolines. The reduced exhaust emissions which have been reported for alcohol-gasoline blends are attributable to the effective leaning of the air-fuel mixture when alcohol is added to gasoline. However, if the AF is not adjusted to compensate for this leaning effect, driveability and performance will suffer. Union Oil Co. (1970) found increased ALDEHYDES with blends and Cevron Research Corp. (1963) found increased FORMALDEHYDE after irradiation with a 25%E blend. At the same Φ HC, CO and NO_x emissions for blends will be same as gasoline while ALDEHYDES and UNBURNED ALCOHOL will be higher.

MATERIALS COMPATIBILITY "Initial use of an alcohol-gasoline blend by the motorist may bring on problems of cleanup and clogged fuel lines. In the longer range view, however, this should present no serious problems; corrosion inhibitors in present day gasolines and modern engine oils could alleviate reported difficulties."

BLEND STABILITY "Alcohol-gasoline-water solubility would present problems of increased handling and cost. Storage facilities would require measures to prevent water contamination because of the hygroscopic characteristic of ethanol. Water tolerance and control would require continuous monitoring to insure against motorists' problems during weather conditions." The solubility of METHANOL in any HC is a function of (a) the HC, (b) temperature, (c) presence of H_2O. Union Oil Co. (1970) reported the following:

% Methanol Soluble	60°F	0°F	0°F, 0.03% H_2O
Aromatic Gasoline	100%		
Regular Gasoline	13%	4%	0.5%
Straight run	4%		

Methanol blended in HC of the same boiling point, is least soluble in normal paraffins, greatest in aromatics and in most cases more soluble in unsaturates than in naphthanes. In all classes of HC solubility decreases with rise in boiling point and molecular weight. Stabilizing compounds are given with iso-butanal being the most effective.

Pefley, R.K., Saad, M.A., Sweeney, M.A. and Kilgrove, J.D. (University of Santa Clara), (125).

PERFORMANCE AND EMISSION CHARACTERISTICS USING BLENDS OF METHANOL AND DISSOCIATED METHANOL AS AN AUTOMOTIVE FUEL

1971 Intersociety Energy Conversion Engineering Conference paper#719008

FUELS 1) Gasoline
2) Blends of CO, H_2 and methanol simulating 0, 30, 70 and 100% dissociated methanol.

ENGINE - CFR with modified carburetor and intake system to allow injection and mixing of methanol.

PARAMETERS, MEASUREMENTS

CR - 8.4,9.2, 10.9		T_{inlet} 40 to 110°F		CO_2
Φ variable		N=900RPM		O_2
SA 0 to 25°BTDC		WOT		NO
ihp	Air Flow	CO-NDIR	Fuel Flow	
HC, Methanol & Aldehydes - GC, sample heated to 110°C				
Aldehydes and Ketones - DNPH				

TEST RESULTS GC - Column - Poropak T satisfactorily separated water, formaldehyde, methanol, acetaldehyde and all HC in the methanol fueled engine (problems discussed).

DNPH aldehyde measurements were erratic.

IHP @ Φ=1

	gasoline	methanol	100% dissoc.methanol
ihp	3.9	3.72	3.15
ratio	1	0.95	0.81

IHP versus Φ essentially the same for methanol and gasoline.

THERMAL EFFICIENCY @ equal Φ essentially the same for methanol and gasoline. At $\Phi < 1$ (lean) gasoline slightly higher η_t; at $\Phi > 1$ gasoline slightly lower η_t than methanol

THERMAL EFFICIENCY for dissociated methanol ≈ 24% versus ≈ 29% for gasoline and methanol @ Φ =1.

HYDROCARBONS Major species were methanol and methane; other HC found only in small concentrations (<40ppm). Total exhaust carbon mass emissions were an order of magnitude lower for methanol than for gasoline @ Φ =1.

NO_x - @ Φ =1, equivalent concentration for gasoline and methanol.

ALDEHYDES Composed almost exclusively of formaldehyde and acetaldehyde. Peak concentrations @ Φ = 0.717 for methanol.

For methanol, @ $\Phi \leq 1$, CR & SA significantly affect aldehydes; in general an increased aldehyde @ high SA (14-25°BTC) was observed.

Dissociation increased aldehyde emission.

CO - @ Φ =1 CO concentration for methanol an order of magnitude lower than gasoline.

O_2, CO_2 with methanol varied with Φ similar to gasoline.

The effects of CR and intake manifold temperature on emission were found to be, with a few exceptions, of secondary importance compared to Φ .

DISSOCIATION: promotes aldehydes; promotes NO_x @ $\Phi < 1$; decreases methanol; promotes methane emission.

Additional comparison are also made between dissociated methanol versus methanol and gasoline. Also, design considerations for decomposing methanol by regenerative heating are presented.

Adelman, H.G, Devoto, R.S., Andrews, D.G., (128).
REDUCTION OF AUTOMOBILE EXHAUST EMISSIONS WITH METHYL ALCOHOL AS FUEL
Dept. of Aeronautics and Astronautics, Stanford University
Final Report Prepared for EPA Contract No. EHSH 71-010, Sept. 1971
Exhaust Emissions From A Methanol-Fueled Automobile SAE Paper 720693

and

Ashby, A.H.
EMISSIONS FROM THE METHANOL FUELED STANFORD UNIVERSITY GREMLIN
Office of Air Programs, EPA August, 1971

FUELS Gasoline and neat Methanol

ENGINE American Motors 232 cu in 6 cyl engine housed in a Gremlin with a 3-speed standard transmission. The carburetor was rejetted to furnish a slightly lean AF and the intake manifold modified for greater heating of charge.

TESTS Various driving cycles (1970FTP, 1972FTP, 9x7 procedure). Constant volume sampling was used to determine emission levels. Tests were also performed with and without an exhaust catalyst with air injection and EGR.

RESULTS

EMISSIONS This car was able to surpass the 1975-76 Federal standards for CO and NO_x while emitting low amounts of unburned HC consisting mainly of methanol which should be lowered by better fuel vaporization.

FORMALDEHYDE concentration (≈ 30ppm) were considerably below that from gasoline fueled automobiles.

Table 7 - Results of Exhaust Analysis for Hydrocarbons and Aldehydes (1972 FTP) Methanol Fuel

	With Catalyst, ppm		No Catalyst, ppm	
Compound	Cold Start	Hot Start	Cold Start	Hot Start
Alcohols				
Methanol	161	29	1580	810
Paraffins				
Methane	6.6	–	7.8	Not measured
Ethane	0.19	trace	trace	trace
N-pentane	0.01	0.15	0.02	trace
Isobutane	0.08	0.13	0.02	0.10
Isopentane	0	0.16	0	0
Olefins				
Ethylene	0.3	0.18	2.1	2.5
Propylene	0.5	–	trace	0.07
Butene-1	0.1	0.01	0.12	0.07
Acetylenes				
Acetylene	0.04	0	0.86	0.58
Aromatics				
None observed				
Aldehydes				
Formaldehyde	33.3	25.6	146.5	131.5
Total aldehydes	36.0	29.2	155.0	144.8
Ammonia				
None observed				

Table 8 - Emission from Methanol and Gasoline-Fueled Gremlin with Hot Manifold (9 × 7 Cold-Start CVS)
with catalyst

Fuel	HC*,+ g/mile	CO, g/mile	Chem** NO_x g/mile	Salt† NO_x g/mile
Gasoline (stock carburetor)	0.28	7.25	2.80	2.41
Methanol (rejetted carburetor)	0.32	3.87	0.39	0.32
1972 Gremlin prototype	2.20	32.5	⟵ 3.2 ⟶	

*FID hydrocarbons reported as $CH_{1.85}$.

**Corrected NO_x as NO_2 measured by chemiluminescence.

†Corrected NO_x as NO_2 measured by Saltzman technique.

+ FID response not corrected for FID methanol sensitivity

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METHANOL is the dominant organic constituent.
FORMALDEHYDE is the dominant aldehyde.
CATALYST on the average: reduced methanol 93%; CO 70%; aldehydes 77%.
NO_x EMISSIONS were found to be predominantly NO.

The low emissions were due to four factors:

1. "The apparently lower (than gasoline) lean misfire limit of methanol, which permits successful operation at $\phi \approx 0.75$, thus reducing HC, CO, and NO_x emissions while maintaining adequate performance.
2. The higher flame speed of methanol, which permits spark retardation to lower NO_x levels.
3. The somewhat lower combustion temperatures (about 180F at the same ϕ) of methanol vis à vis HC fuels, which slows the rate of formation of NO, thus reducing NO_x.
4. The use of a catalytic muffler with air injection to reduce HC and CO concentrations further in the exhaust gas after it leaves the engine."

INTAKE MANIFOLD MODIFICATION A heat exchanger using engine cooling water which was fitted to the carburetor adaptor plate proved adequate at idle and low-speed cruise but inadequate during high speed.

FUEL ECONOMY @ high speed cruise (70 mph): 18 mpg G;9-10 mpg M.

CRUISE AND ACCELERATION A water heated intake manifold was installed with the heat riser valve permanently closed. This improved performance and emissions but maldistribution was still present. A switch to exhaust gas heating was necessary because of the time required for the cooling water heated intake manifold and heat exchanger to reach operating temperature. An exhaust gas heated intake manifold gave satisfactory performance without the heat exchanger but the heat exchanger still made a measureable contribution to HC and CO emissions reduction.

STARTING Equilibrium AV calculated indicating starting difficulties with Methanol @ $T < 77^{\circ}F$. Their experience showed this to be the case.

THEORETICAL CONSIDERATIONS -
Frozen Nitric Oxide Concentrations (ppm, wet basis)

ϕ	RPM	ISOOCTANE	METHANOL
1	2400	5000	3900
1	3600	5000	4100
0.75	2400		2000
0.75	3600		1400

Ebersole, G.D. and Manning, F.S. (University of Tulsa), (129).
ENGINE PERFORMANCE AND EXHAUST EMISSIONS: METHANOL VERSUS ISOOCTANE
SAE 720692, August, 1972

FUELS Isooctane and neat Methanol

ENGINE CFR engine with vaporized fuel by mixing with 180°F air.

PARAMETERS, MEASUREMENTS

Φ	Air Flow	Lean limit misfire
N	Fuel Flow	CO, CO_2 - NDIR
CR	SA - Max Power	HC - FID, 40% H_2 - 60% He Fuel
imep	sfc	O_2 - Polarographic technique
N=1000 & 1800RPM	$T_{coolant} = 149^{\circ}F$	NO - Saltzman method
	$T_{mixture} = 125^{\circ}F$	Aldehydes - MBTH

TEST RESULTS LEAN LIMIT MISFIRE considerably leaner (about 0.2 equivalence ratios) for methanol.

HC - @ comparable imep and Φ, HC mass emission lower by nearly an order of magnitude.

CO mass emissions become essentially zero at same Φ as with isooctane and increase with increasing Φ at a lower rate for the methanol.

NO trends same as isooctane by somewhat lower mass emission (one-half @ midrange imep). Lower NO emission possible because of allowable operation at lean mixtures.

ALDEHYDES with methanol generally higher mass emissions at comparable imep and Φ. Also aldehydes are affected more by Φ than isooctane.

ISFC average 2.15 times that of gasoline.

EFFICIENCY with methanol 5% greater at 1000RPM, 4% greater at 1800RPM.

Spark retard data also presented for both fuels.

Maximum power nearly equal for both fuels.

TEXACO (Texaco Research Center, Beacon, N.Y.) , (134).

EVALUATION OF METHANOL AS A COMPONENT OF MOTOR FUEL

FUELS Various commercial gasolines (89.6-94 RON; 80.7-84 MON) and various blends of refinery stocks plain and with 10% and 20% (vol.) methanol.

ENGINES CFR; Single Cylinder RHD engine with manifold fuel injection; 1970 and 1971 vehicles.

TESTS Engine Dynamometer and Chassis Dynamometer

MEASUREMENTS, PARAMETERS

RON	Road ON	Fuel Consumption	Storage
MON	Co-NDIR	Blend"leaning effect"	Water Tolerance
imep	HC-FID	Carburetor jets	Corrosion
ϕ	NO_x-Salzman	Cylinder p vs. t	ASTM Distillation
Methanol and HC by GC			RVP

TESTS RESULTS

OCTANE - Research gain of methanol greater than motor gains. Best response found in low octane paraffin-aromatic stocks. Some octane antagonism with olefins. Positive deviation of MON from linear suggests an optimum addition rate of 10%. Shows that blend leaning effect will give an apparent (but false) increase in octane quality.

BLEND LEANING EFFECT results in poor performance which can be regained only with changes in carburetion not necessarily limited to merely enlarging the main metering jets as was found to be sufficient for one vehicle.

PEAK CYLINDER PRESSURE for a 20% blend occurs ≈ 4 crank angle degrees later than gasoline indicating slower blend flame speeds. This probably caused the 100°F higher exhaust temperature observed with the blend. The peak pressure (and temperature) levels for blend same as gasoline thus indicating that the superior anti-knock quality of blend is not due to a cooling of end gas effect.

IMEP essentially same for 20% blend and gasoline @ equal ϕ.

ISFC 15% higher for 20% blend @ same ϕ as gasoline (volume consumption 12% higher).

EXHAUST EMISSIONS @ same ϕ : essentially the same CO, NO_x and total HC concentrations as for gasoline with a 20% blend. For $\phi \geq 1$, however, HC for blend is less. There were also some differences in hydrocarbon species as determined by the GC analysis:

$ppmC_6$	Gas.	20%B	Ratio
Methane	95.2	48.1	0.51
Ethane	176.9	168.1	0.95
Propylene	16.7	18.9	1.13
Isobutylene	2.7	2.5	0.93
Acetylene	166.7	71.2	0.43
Butane	7.0	8.0	1.14
Isopentane	21.8	21.4	0.98
Methanol	0	7	

$ppmC_6$	Gas.	20%B	Ratio
Isooctane	15.1	19.0	1.26
Benzene	30.4	22.4	0.74
Toluene	79.0	68.8	0.87
C_8 Aromatics	203.0	170.2	0.84
Other C_4-C_8 Olefins	14.6	13.1	0.88
Other C_2-C_8 Paraffins & Naphthenes	83.2	85.1	1.02

ASTM DISTILLATION CURVE exhibits midrange depression (≈ 90°F @ 50% point). Concludes that even 10% blends will have difficulty meeting vapor lock specifications.

WATER TOLERANCE in storage is a significant problem. Storage tests suggest normal "breathing" of a fixed roof tank can result in separation. Conclude that extensive modifications of fuel handling systems, are required.

WATER TOLERANCE STABILIZING Additives are relatively ineffective and require large amounts of additive. Water tolerance better for high aromatic gasolines.

CORROSION of copper or brass was identified as a potential problem with the blend.

TABLE V

VEHICLE EMISSIONS TEST RESULTS

Federal Test Procedure - Hot Cycle

Vehicle	Carburetor Jets	Fuel	Hydro-carbon	CO	NO_x
1970 Car A	0.048 in.	Base Gasoline	2.04	39.65	5.59
302 cu. in. V-8	0.048 in.	20% Methanol	1.58	18.70	4.47
	0.053 in.	20% Methanol	2.27	38.98	-
1971 Car B	0.058 in.	20% Methanol	1.89	9.32	4.77
350 cu. in. V-8	0.064 in.	20% Methanol	2.54	26.40	6.20
1970-71 Standards			2.2	23.0	4.0
1976 Standards			0.41	3.4	0.40

Rogers, J.D., Jr., (144).
ETHANOL AND METHANOL AS AUTOMOTIVE FUELS
E.I.DuPont De Nemours & Co., Inc.
Petroleum Chemicals Division, Petroleum Laboratory Report P813-3, Nov.73.

This report is a good review of the use of ethanol or methanol as automotive fuels or as blending components in gasoline. The conclusions drawn are based on data published elsewhere and thus are only summarized here (omitting economic considerations covered in the report).

EMISSIONS of CO, HC and NOx with blends are similar to conventional gasolines. Increased aldehydes and unburned alcohol are emitted with blends.

OCTANE blending values of ethanol and methanol are beneficial in low octane, unleaded gasoline. Blending values diminish with an increase in octane level, particularly the Motor Method. Road octane response of alcohols in premium gasoline is small.

DRIVEABILITY would deteriorate unless carburetors are enriched with blends.

The report also summarizes previously obtained data with neat alcohol fuels.

Adt, R.R., Jr., Greenwell, H. and Swain, M.R. (University of Miami) , (155).
THE HYDROGEN AND METHANOL FUELED-AIR BREATHING AUTOMOBILE ENGINE
The Hydrogen Economy Miami Energy (THEME) Conference, March, 1974

FUELS 1) Methanol Neat
2) Hydrogen (not discussed here)

ENGINE 4 cylinder, Pontiac engine, CR=10

TESTS Engine Dynamometer

PARAMETERS, MEASUREMENTS

N = 1450 RPM	SA - variable	CO
Torque - variable	η_b	HC*
ϕ - variable	NO_x	

RESULTS (METHANOL)

LEAN LIMIT $\phi \simeq 0.78$ @ N = 1450RPM, T=15ft.lb.

EFFICIENCY η_b increased from ≃9% @ $\phi=1$ to ≃12% @ lean limit.

NO_x PEAKS @ $\phi=0.92$.

NO_x vs.spark advance trend similar to gasoline.

HC decrease with leaning of mixture until $\phi \simeq 0.8$ then found to increase.

CO levels approach $< 0.1\%$ @ $\phi \leq 0.85$.

METHANOL offers an advantage over gasoline in that it can be used @ leaner AF which in turn increases η_b and reduces exhaust emissions.

MIXTURE HEATING To maximize heat transfer to the intake manifold hot spot the entire exhaust flow was passed through the intake manifold crossover duct.

DISTRIBUTION problems were still present. The manifold mixture temperature was not uniform.

LOWER LEAN LIMIT OF COMBUSTION ϕ attributed to high methanol flame speeds.

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* Hydrocarbons measured with unheated FID with condenser bath in sample stream. FID output not corrected for relative response.

Ingamells, J.C. and Lindquist, R.H., (170).
METHANOL AS A MOTOR FUEL
Engine Fuels Division, Chevron Research Co. May, 1974

FUELS 1) Commercial unleaded base gasoline
2) Methanol
3) 10% Blends

ENGINES Various-housed in 1967-1971 vehicles and octane rating engine

TESTS Chassis Dynamometer and Road Tests

MEASUREMENTS

RON	Fuel Economy	Exhaust Emissions - neat methanol
MON	Driveability	Water Sensitivity
Road ON	Cold Starting	Materials Compatibility

TEST RESULTS

	RON	MON	ROAD
Gasoline	91.1	82.5	89.2
10% Blend	95.5	84.5	92.0

1971 Car Make	Car Size	$\frac{(\text{mpg})_G}{(\text{mpg})_B}$	$\frac{(\text{BTU/mi})_G}{(\text{BTU/mi})_B}$
A	Full	1.05	1.03
B	Medium	1.01	1.07
B	Full	1.04	1.04
C	Compact	1.03	1.05
C	Medium	1.06	1.02

This table shows an increased volume consumption but a decreased BTU consumption for the blend as compared to gasoline

DRIVEABILITY demerits higher for the blend. Acceptable in two cars; three cars with reasonable driveability on gasoline became poor with blend; one car deteriorated from poor to very poor on switching to blend. Decrease in driveability more pronounced during -4°C(24.8°F) chassis dynamometer tests (see next page).

COLD STARTING tests with 1971 (make D) car running on methanol would exhibit acceptable starting only if 10% butane or 20% isopentane was used when temperatures were below 15°C (59°F).

EXHAUST EMISSIONS with a standard exhaust system exhibited, over a 23 minute city driving cycle, more unburned fuel and CO with methanol, aldehydes about same and nitrogen oxides lower.

EXHAUST EMISSIONS with a catalytic reactor and exhaust port air injection were the same or considerably lower with methanol (aldehydes not compared).

WATER SENSITIVITY
Will necessitate a completely revamped fuel distribution system.
Presents haze point measurements at 21°C (69.8°F) and 3°C (37.4°F).
Examined over 150 water solubilizing additives and found none effective at reasonable additive concentration.
Most effective additives the higer alcohols but cost prohibitive.
Conclude car fuel tank and carburetor bowl would have to be vented through drier to minimize moist air intrusion.

MATERIALS COMPATIBILITY
Blends attack terneplated steel forming lead hydroxide which can plug fuel filter and carburetor.
Subsequent corrosion of underlying steel presents a problem.
Nine classes of corrosion inhibitors at the 1000ppm level not effective in M or 50% M blend.
Electric fuel pump sets up electric potential resulting in rapid electrolytic attack on fuel tank's lead coating.

MATERIALS COMPATIBILITY (Cont'd.)

Magnesium found to be susceptible to M corrosion.

Some fuel system elastomers expanded and/or softened in M.

Conclude Methanol is not a useful fuel additive for unmodified cars. Also points out that while the required 60% carburetor enrichment required for a 10% blend is not mechanically difficult problems may arise with EPA certification.

Driveability Tests

1971 Car Make	Car Size	Driveability Demerits No Methanol*	 10% Methanol
	Commuting at 4°C to 21°C		
A	Medium	12.3	24.0
A	Full	6.0	15.5
B	Medium	3.8	4.3
B	Full	8.5	15.3
C	Compact	4.8	10.8
C	Medium	2.5	3.8
	Chassis Dynamometer at -4°C		
A	Full	7	11
B	Medium	3	12
C	Medium	4	22

*Commercial unleaded base gasoline.

Jackson, R.G. and Tillman, R.M. (Continental Oil Co.) , (171).
AUTOMOTIVE USES OF METHANOL FUEL
COAL-DERIVED METHANOL AS MOTOR FUEL
Engineering Foundation Methanol Conference, July, 1974.

This paper addresses the U.S. energy situation and the conversion of coal to methanol and SNG as well as the topics outlined below. Introductory remarks include the following:

At 5-7% v methanol little difference would be noted by driving public.
In an unleaded 91 ON Fuel BOV = 133R and 100M. Thus 5% methanol would increase RON by 2 and MON by 1.
Slight 2-2½% loss in fuel economy on a gallon basis.
Fuel economy on a BTU basis would not diminish.
Solubility of 5 to 7% M not a problem at normal aromatic level gasoline.
Main problems 1) water and separation
2) materials compatibility
Higher M levels of 10-30% offer little incentive.
Consider blending a waste, better to use methanol neat.

FUELS 1) Gasoline
2) Methanol

ENGINE 1973 Ford 302 cu.in. V-8.

TESTS Engine Dynamometer at variable RPM (30-70mph) and at road load and maximum power.

MEASUREMENTS, PARAMETERS

bhp	(BTU/HR)/HP	Range (20 gal.tank)
bsfc	mpg	NO_x - ppm
	CO	HC - ppm

TEST RESULTS

NO_x concentration for M @ road load 3 to 4 times lower than gasoline.
HC concentration* for M @ max power about 3 to 4 times lower
HC concentration* for M @ road load about same as for gasoline at 30mph. As mph increases gasoline HC increased while M remains same until at 70mph gasoline HC about 3 times that of methanol.
BSFC methanol about twice that of gasoline.
BTU consumption [(BTU/HR)/HP] for methanol 18 to 28% less @ max power and 15 to 26% less @ road load.
BTU consumption at 50mph and equivalent NO_x for methanol is 41% less (70% less @ 70mph).

	Methanol			Gasoline		
mph	mpg	$(BTU/mi)_R$	Range	mpg	$(BTU/mi)_R$	Range
30	12.4	0.32	247mi	20.4	1.00	409mi
50	11.6	0.87	233mi	19.9	1.03	398mi
70	10.3	0.98	206mi	15.7	1.30	315mi

Range for a 20 gallon tank

$$(BTU/mi)_R = \frac{(BTU/mi)}{(BTU/mi)_{gasoline@30\,mph}}$$

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* HC data corrected for FID methanol response but do not include formaldehyde emission.

RVP methanol = 3psi
Cold starting a problem at temprature below 55°F with M. Addition of 3% butane raised RVP to 12psi and permitted cold starting at as low as 10°F.
Distribution poor with conventional manifold with M.
Optimum spark curve not same as gasoline.

MATERIALS COMPATIBILITY Found sticking of viton float valve seat with M.

Reed, T.B., Lerner, R.M., Hinkley, E.D. and Fahey, R.E. (M.I.T.) , (176).
IMPROVED PERFORMANCE OF INTERNAL COMBUSTION ENGINES USING 5-30% METHANOL IN GASOLINE
Engineering Foundation Methanol Conference, July, 1974

FUELS 5-30%(v) methanol in gasoline

ENGINES Various housed in 1968 through 1974 vehicles.

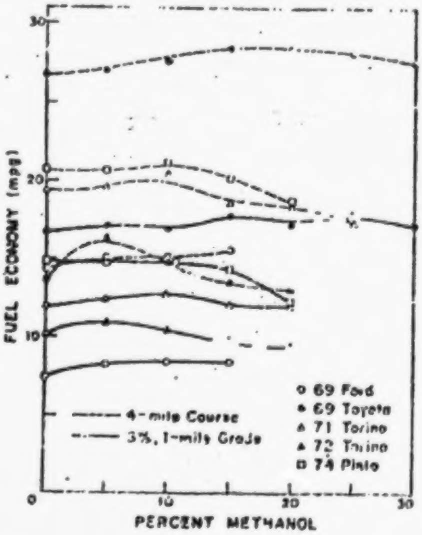
TESTS Road Tests

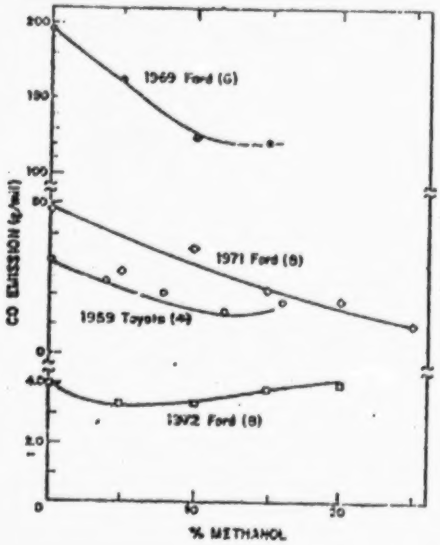
PARAMETERS, MEASUREMENTS

mpg	RON	Driveability
CO	Blend Stability	Starting
RON	Exhaust Temperature	Warm up

FUEL CONSUMPTION ECONOMY (mpg) was comparable or improved with M addition up to at least 10%(v) for all cars tested and generally decreased at higher concentration

CO EMISSIONS decreased 20-70%. The smallest decrease was for a 1972 Ford which had lowest CO to start with.





EXHAUST TEMPERATURES fell 10-50°C (50-122°F) in all cases.

NO ENGINE TROUBLES encountered in over 10,000 mi using various M-mixture and gasoline in a 1969 Toyota (CR=8).

ACCELERATION TIME for 0-60mph decreased from 21.4 to 20.0 seconds for 5% blend (69 Toyota).

DRIVEABILITY not adversely affected for under 20% blends (69 Toyota).

HESITATION @ IDLING noted for 30% blend (69 Toyota).

DRIVEABILITY @ 50% blend - 69Toyota unpleasant to drive.

KNOCK observed in 69 Toyota with gasoline; no knock with 5% or greater blend.

DIESELING after turning ignition off disappeared with 5% or greater blend (71 Ford V8, CR=9).

STARTUP with 10% blend in winter seemed improved (69 Toyota).

WARMUP with 10% blend rough operation was observed for a few minutes when temperature was below 20°F (-6.7°C).

SYNERGISTIC EFFECTS Disproportionate improvements in economy and octane attributed to synergistic effects of: (1) blend leaning and (2) decomposition during compression. The decomposition of methanol takes place close to autoignition temperature of gasoline (220°C, 428°F) and can quench the chain reaction. The CO and H_2 produced increases burning velocity giving more complete combustion and making leaner mixtures more combustible.

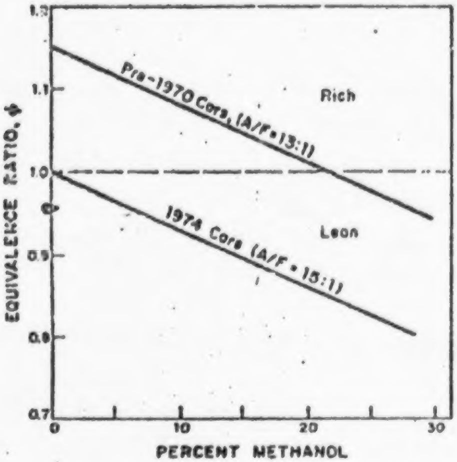


Fig. 7. - Chemical leaning produced by addition of methanol to gasoline.

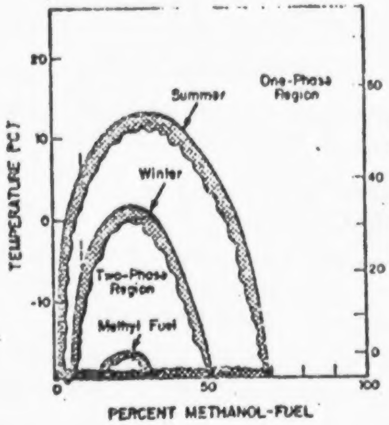
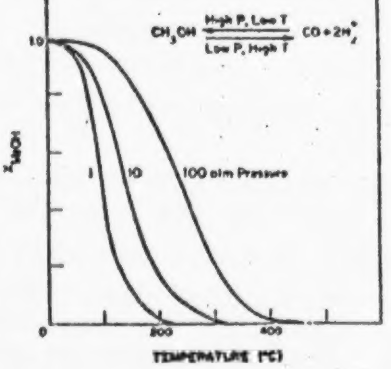


Fig. 5. - Temperature separation of methyl-blends in winter and summer gasoline.



Equilibrium between methanol and synthesis gas.

Bernhardt, W.E. and Lee, W. (Volkswagen), (158).
COMBUSTION OF METHEL ALCOHOL IN SPARK IGNITION ENGINES
15th International Symposium on Combustion, Tokyo, Japan Aug.15-31, 1974

FUELS 1) Gasoline - premium grade
2) Methanol

ENGINES 1) 4 cylinder, water-cooled 1.6 Liter, Volkswagen engine
2) CLR

TESTS Engine dynamometer

ENGINE MODIFICATIONS Improved atomization carburetor.
Extra exhaust gas heating pipes in intake manifold.

PARAMETERS, MEASUREMENTS

WOT	T_{mix}	CO- NOIR
1000-5000RPM		HC - FID
ϕ variable	η_i	NO_x - Chemiluminescent
SA -best power	ihp	
Air Flow	GC - HC, Meth., Aldehydes	
Fuel Flow	Water addition to methanol	

THEORETICAL CONSIDERATIONS

POST FLAME GAS TEMPERATURE found to be ≈ 250°K(450°F) lower than gasolene @ Φ= 1.06, N=3010RPM, 7.88CR; max power SA and WOT.

NO_x FORMATION via $N_2 + O \rightarrow NO + N$ is restrained due to less available atomic oxygen @ the lower post flame temperature.

FORMALDEHYDE the authors point out, is an important intermediate product as indicated by cool flame bands observed (by others) during methanol combustion.

REACTION MECHANISM is presented which accounts for the main products in methanol fueled engine exhaust.

WATER ADDITION results in formation of hydroxyl radical $H_2O + O \rightarrow OH + OH$ which in turn reacts with and thus reduces formaldehyde, $HCHO + OH \rightarrow H_2O + HCO$.

The production of OH from H_2O and O thus reduces available O for formation of NO.

TEST RESULTS

MIXTURE TEMPERATURE - Gasoline ≈ 25°C (77°F). Methanol between 7°C (45°F) @ 5000RPM and 19°C (66°F) @ 1000RPM with additional heating of methanol mixture.

IHP approximately 10% greater for M @ near ϕ =1, max. power SA, CR = 9.7.

INDICATED THERMAL EFFICIENCY - an average increase of 14% over gasoline for the speed range tested @ max power SA, CR = 9.7.

BSFC Average increase of 92% for above conditions.

NO_x CONCENTRATION data found to be predictable by a simple model which consists of (1) thermodynamic analysis based on a two-zone model of flame propagation and (2)the Zeldovich reaction mechanism.

NO_x CONCENTRATION found to be ≈ ½ that of gasoline near $\phi \leq 1$.

CO CONCENTRATION for Methanol approaches zero @ $\phi \leq 1$ and rises less rapidly with increasing ϕ .

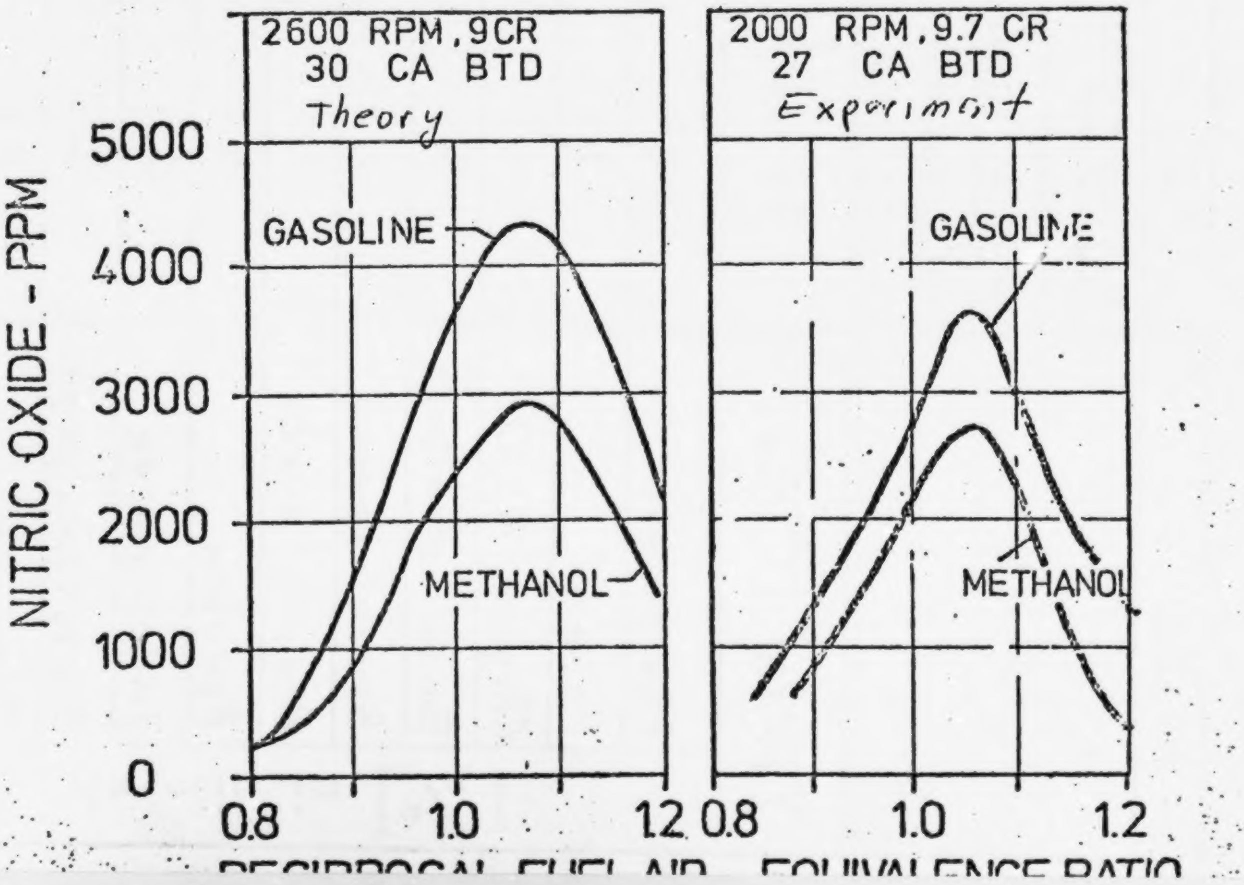
GC ANALYSIS - EUROPEAN TEST PROCEDURE

Species	wt% of Total HC + Meth.	Species	wt%
Methanol	88.3	ethyl benzene	0.2
C_1, C_2, C_3, C_4 compounds	4.0	xyloles	2.1
pentanes	1.1	propylbenzene	1.3
hexanes	1.5	pseudo cumole	0.8
toluole	0.3	higher HC	0.4
		Formaldehyde-20ppm	

CR = 9.7, N = 2000RPM, WOT, best power SA			
ppm (C_6)	HC	HC + Methanol	Total Aldehydes
$\phi = 1$	50	164	77
$\phi = 0.75$	14	143	97

WATER ADDITION Reduces NO & Aldehydes. For greater than 10%(v) H_2O, however, FID HC found to increase. At 10% (v) H_2O, NO reduced to 1300ppm from 3100ppm with 0% H_2O and aldehydes reduced to 35ppm from 64ppm with 0% H_2O.

WIDE OPEN THROTTLE & MAX POWER SPARK TIMING



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Versuch		I.	II.	III.
2.5'8 miles VW Dasher ECE-Test results:		Passat LS DASHER abgestimmt auf Methanolbetrieb Wagen 400-716 2060 Km	Passat LS Serie 15% Methanol + ERF-G1 Wagen 400-622 15346 Km	Passat LS Serie ERF-G1 Wagen wie II. 15351 Km
Σ PAKW [µg/Test]		303,6	888,5	1070,4 *
Anteile in [%]	Fluoranthen	39,4	27,4	24,4
	Pyren	39,6	41,5	32,7
	Chrysen + MS 226	6,6	5,2	6,5
	Benzofluoranthene	3,9	3,5	4,9
	Benzo(e)pyren	1,5	3,3	4,5
	Benzo(a)pyren	1,0	2,3	3,1
	Perylen	0,1	0,4	0,4
	Indenopyren	2,1	4,1	6,1
	Benzo(g,h,i)perylen	3,5	7,4	10,9
	Coronen	2,5	4,9	6,5
		Analyse Gr.	Analyse ZL	Analyse ZL

* normal up to 10,000 µ;

Lange, I. and Dusan, G. "Verbrennungsablauf und Abgasemission in einem Motor mit dem Porsche - Schichtlade - Kammer - System 2nd Symposium on Low Pollution Power Systems Development", (193). Dusseldorf, Neue Messe, November 4-8, 1974. (Note: $\lambda_{ges} = 1/\Phi$)

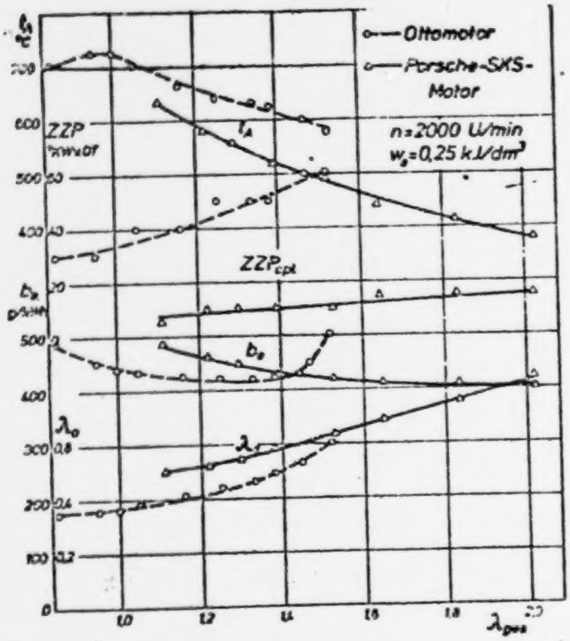


Bild 5 Vergleich der Verbrennungsverfahren.

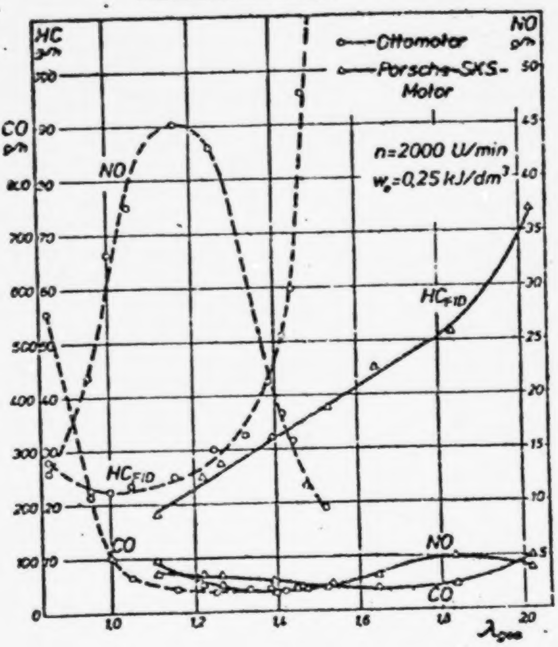
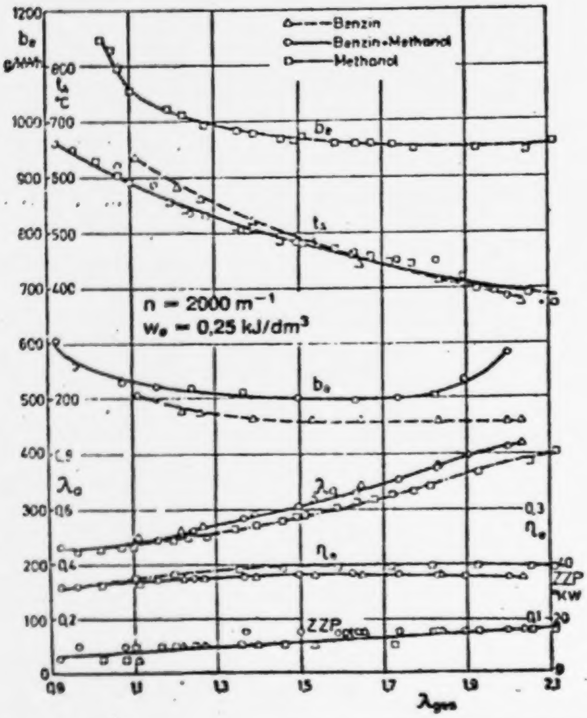


Bild 6 Vergleich der Verbrennungsverfahren.



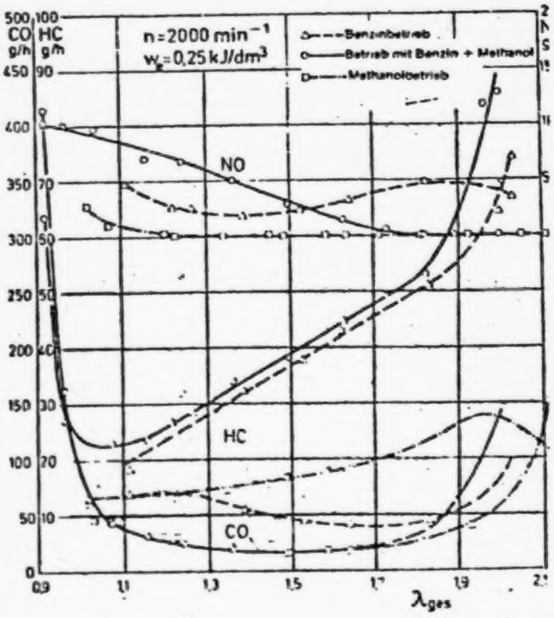


Bild 87: Abgasemission des Porsche-SKS-Motors